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Reactions of Hexachlorocyclotriphosphazene and Lewis Bases to Produce [PON]₃: Methanesulfonic Acid and Dimethylformamide Reactions with [PCl₂N]₃

Savannah R. Snyder

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ABSTRACT: Several chlorine/oxygen exchange reactions of $[\text{PCl}_2\text{N}]_3$ were investigated with the goal of forming $[\text{PON}]_3$, a precursor to PON materials. The reaction of MeSO_3H and Et_3N with hexachlorocyclotriphosphazene ($[\text{PCl}_2\text{N}]_3$) has been claimed to produce a $[\text{PON}]_3$ single molecule. This reaction could not be reproduced. Only partially oxygenated phosphazenes have been obtained. Similarly, in the reaction of $[\text{PCl}_2\text{N}]_3$ and dimethylformamide (DMF) both partial and full oxygenation occurs. Stoichiometry appears to be crucial in determining the species that is produced in both reactions. These products were characterized by multinuclear NMR spectroscopy.

i. Introduction

Phosphazene materials are said to “represent one of the most interesting and promising inorganic systems” due to their applications in fire retardancy as well as drug delivery systems.¹ The structures of phosphazenes consist of alternating phosphorus and nitrogen atoms and are of much interest in the inorganic field. $[\text{PCl}_2\text{N}]_3$ (**1**) is a cyclic polyphosphazene that is obtained in highest yield during phosphazene ring synthesis, and it is also known as phosphonitrilic chloride trimer in the older literature. Chlorine atoms are found on the phosphorus atom of $[\text{PCl}_2\text{N}]_3$. In the research described below, which was done in collaboration with Ben Thome in the laboratory of Professor Claire Tessier, these chlorine atoms were to be substituted with oxygen atoms resulting in $[\text{PON}]_3$ (**2**).

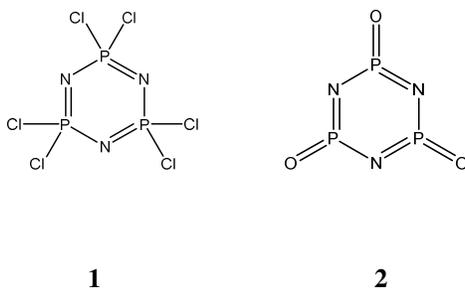
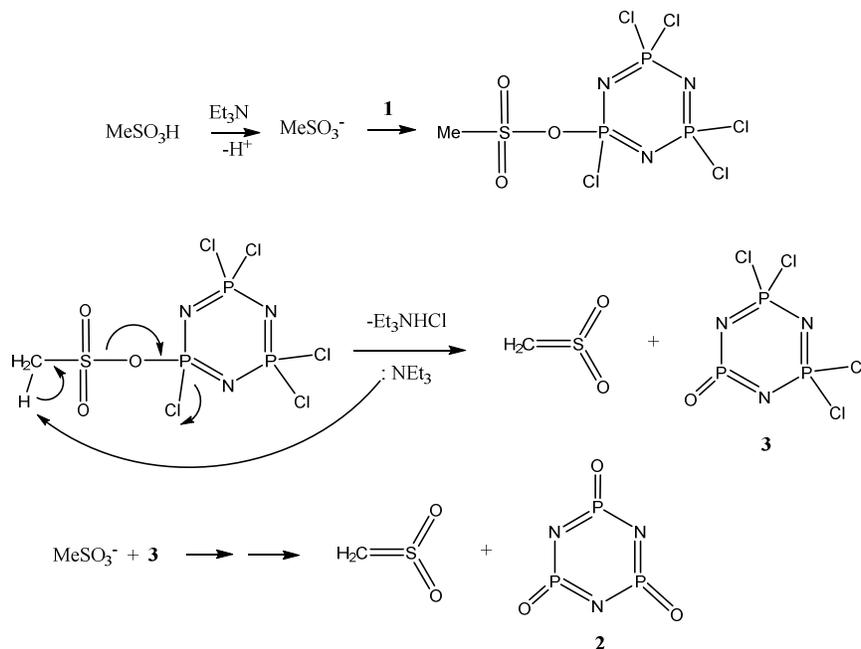


Fig. 1 Molecular structure of phosphonitrilic chloride $[\text{PCl}_2\text{N}]_3$ (**1**) and oxygen substituted $[\text{PON}]_3$ (**2**).

Compounds of formula PON have been mentioned in the literature several times. A three-dimensional solid of the formula $[\text{PON}]$ does exist.² The trimeric molecule $[\text{PON}]_3$ has been recorded as a bi-product, but without

substantial evidence,³ while other literature indicates the molecule is stable enough to exist through computational chemistry,⁴ and its metal complexes can be isolated.⁵ Many potential applications have been proposed for these phosphoryl oxynitride solids, including as a passivating coating on InP surfaces and flame retardants in plastics manufacturing.⁵ However, in reference to the goals of this research, the synthesis and isolation of a single-molecule [PON]₃ is strived for.

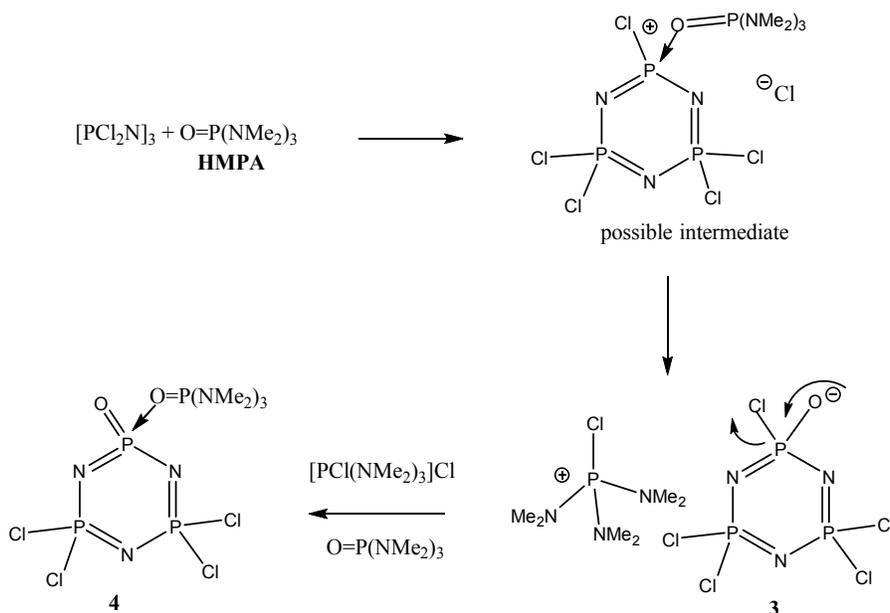
Zarei and coworkers indicate that the isolation of [PON]₃ is successful (Scheme 1), but only as a bi-product, and therefore no spectra were recorded.⁶ Zarei's synthesis is done by first using a Brønsted base, triethylamine, to deprotonate a sulfonic acid (RCH₂SO₃H, R = Me, Et...). The anion is utilized in a nucleophilic reaction and substitutes the chlorine atoms of the ring by the moiety itself attaching to the ring by the oxygen atom. Nucleophilic attack by the triethylamine causes a double bonded oxygen and a low molecular weight sulfene. Further reaction produces the fully oxygenated [PON]₃. In the subsequent reactions done methanesulfonic acid was used, which provides the adjacent hydrogen necessary in order for the reaction to be carried out.



Scheme 1. Proposed mechanism by Zarei and coworkers for the conversion of [PCl₂N]₃ to [PON]₃.

Zarei's work involves chlorine/oxygen exchanges processes, which have been of interest in the Tessier group. In unpublished work from the Tessier group headway has been made on the subject and partial substitution of the chlorides of [PCl₂N]₃ can be made using OP(NMe₂)₃ and HCONMe₂ as sources of oxygen atoms. As an example, Scheme 2 shows the former chlorine/oxygen exchange where [PCl₂N]₃ was reacted with HMPA resulting in loss of

a chlorine and addition of an oxygen atom to the ring. Further reaction can cause a second loss of chlorine and complexation of HMPA to the Lewis acidic phosphorus atom of the P=O group. In some cases, further reaction does not occur. However, only partial substitution of an oxygen atom or oxygen atoms of $[\text{PCl}_2\text{N}]_3$ has been observed to date.



Scheme 2: Proposed mechanism of the reaction of $[\text{PCl}_2\text{N}]_3$ with HMPA (unpublished work by Benjamin Thome and Joanna Beres). Both $[\text{PCl}(\text{NMe}_2)_3][\text{POCl}(\text{PCl}_2)_2\text{N}_3]$ and $[\text{PO}(\text{HMPA})(\text{PCl}_2)_2\text{N}_3]$ were isolated and characterized.

The proposed research will investigate Zarei's work, but focus on isolation of the $[\text{PON}]_3$ single molecule system. As mentioned previously, a goal of this work is to isolate $[\text{PON}]_3$ from chlorine/oxygen exchange reactions of $[\text{PCl}_2\text{N}]_3$. In addition to work related to Scheme 2, other sources of oxygen atoms for chlorine/oxygen exchange reactions of $[\text{PCl}_2\text{N}]_3$ will be examined.

ii. Methods and Materials

General Procedure: All glassware was dried in an oven overnight (120 °C) before use and all apparatus were assembled hot. Standard anaerobic techniques were used.⁸ Dichloromethane, chloroform, hexanes and acetonitrile (Fischer Scientific) were dried and deoxygenated by copper and alumina columns in the PureSolv solvent systems

(Innovative Technologies Inc.). $[\text{PCl}_2\text{N}]_3$ (Sigma Aldrich) was used as received. Triethylamine (Sigma Aldrich) was dried over P_2O_5 , distilled onto 4 μ sieves, and stored under nitrogen atmosphere. MeSO_3H (Sigma Aldrich) was dried by azeotropic distillation with toluene and degassed. Routine NMR spectra were obtained using a Varian Gemini 300 MHz, a 400 MHz Varian INOVA and VNMRS 500 MHz instruments at 25 $^\circ\text{C}$. ^{31}P NMR were referenced to an external reference of 0.15 M H_3PO_4 solution in a deuterated solvent (0 ppm). ^1H NMR and ^{13}C NMR were referenced to the residual protons (7.24 ppm) and the ^{13}C atoms (77.23 ppm) in CDCl_3 solvent.

Reactions of $[\text{PCl}_2\text{N}]_3$, MeSO_3H and NEt_3

Et_3N (0.6974 mL, 5.000 mmol) was added to $[\text{PCl}_2\text{N}]_3$ (0.1758 g, 5.057 mmol). MeSO_3H (0.3247 mL, 5.000 mmol) and CDCl_3 were added to a 150 mL Schlenk flask. The solution was stirred magnetically for 23 hours. The volatile components were removed using the Schlenk line and the brown, oily product characterized by ^{31}P NMR in CDCl_3 (Fig. 4). ^{31}P NMR (CDCl_3) δ (ppm): 0.5 (t), -11.4 (t), 20.8 (d), 20.9 (d), 19.9 (s).

A 150 mL Schlenk flask was equipped with a stir bar and CH_2Cl_2 (10 mL) and placed in a glove box. Et_3N (0.419 mL, 3.01 mmol) and MeSO_3H (0.195 mL, 3.00 mmol) were added to the flask. The mixture was stirred for an hour. $[\text{PCl}_2\text{N}]_3$ (0.3487 g, 1.003 mmol) was added. The mixture was stirred for 20 hours. The volatile components were removed using the Schlenk line and the oily, brown product was characterized by ^1H , ^{31}P and ^{13}C NMR (Fig. 5, 6). ^1H NMR (CDCl_3) δ (ppm): 9.79 (s), 3.52 (s), 2.93 (t), 2.44 (s), 1.11 (t). ^{31}P NMR (CDCl_3) δ (ppm): -11.3 (t, J = 54 MHz), -1.0 (t, J = 42 MHz), 19.9 (d, J = 53 MHz), 20.0 (d, J = 43 MHz). ^{13}C NMR (CDCl_3) δ (ppm): 8.6 (s), 39.4 (s), 39.7 (s), 46.0(s), 52.7 (s), 77.3 (t).

In the glove box, Et_3N (0.419 mL, 3.00 mmol) and MeSO_3H (0.195 mL, 3.00 mmol) were added to a 150 mL Schlenk flask, equipped with a stir bar. The solution was stirred for 25 minutes. Using Schlenk techniques, $[\text{PCl}_2\text{N}]_3$ was added (0.3479 g, 1.001 mmol) and a condenser and a bubbler were attached to the flask. The mixture was refluxed for 20 hours. The volatile components were removed using the Schlenk line. In the glove box, an NMR sample was prepared of the brown, oily solid. Acetonitrile (10 mL) and hexanes (10 mL) were added to the reaction flask and stirred for 15 minutes. The contents of the reaction flask were transferred into the separatory funnel. The acetonitrile layer and hexanes layer were separated into two different Schlenk flasks. The volatile components were

removed from each flask using the Schlenk line. The black, viscous product was characterized by ^{31}P NMR (Fig. 14). ^{31}P NMR δ (ppm): -11.6 (t, J = 57 MHz), -1.0 (t, J = 45 MHz), 20.7 (d, J = 58 MHz), 20.8 (d, J = 46 MHz).

A 150 mL Schlenk flask was equipped with a small stir bar and methylenechloride (4 mL) in the glove box. Triethylamine (0.279 mL, 2.00 mmol) and methanesulfonic acid (0.130 mL, 2.00 mmol) were added to the flask. The solution was stirred for 1 hour. $[\text{PCl}_2\text{N}]_3$ (0.3475 g, 1.000 mmol) was added and the solution was stirred for 20 hours. The brown, oily product was characterized by ^{31}P NMR (Fig. 9). ^{31}P NMR δ (ppm): -11.8 (t, J = 58 MHz), -0.8 (t, J = 46 MHz), 19.9 (s), 20.8 (d, J = 57 MHz), 20.9 (d, J = 45 MHz).

A 150 mL Schlenk flask was equipped with a small stir bar and methylenechloride (10 mL). Triethylamine (0.1395 mL, 1.002 mmol) and methanesulfonic acid (0.0650 mL, 1.00 mmol) were added in the glove box. The solution was stirred for 40 minutes. $[\text{PCl}_2\text{N}]_3$ (0.3484 g, 1.000 mmol) was added and the solution was stirred for 20 hours. The volatile components were removed on the Schlenk line. The brown, oily product was characterized by ^{31}P NMR (Fig. 8). ^{31}P NMR δ (ppm): -10.8 (t, J = 57 MHz), 0.0 (t, J = 45 MHz), 20.0 (s), 21.2 (d, J = 59 MHz), 21.1 (d, J = 45 MHz).

A 150 mL Schlenk flask was equipped with a small stir bar and methylenechloride (10 mL). Triethylamine (0.837 mL, 6.01 mmol) and methanesulfonic acid (0.390 mL, 6.01 mmol) were added in the glove box. The solution was stirred for 40 minutes. $[\text{PCl}_2\text{N}]_3$ (0.3479 g, 1.000 mmol) was added and the solution was stirred for 20 hours. The volatile components were removed on the Schlenk line. The brown, oily substance was characterized by ^{31}P NMR (Fig. 10). ^{31}P NMR δ (ppm): -12.4 (t), -2.0 (t), 20.07 (d), 20.11 (d). Acetonitrile (10 mL) and hexanes (10 mL) were added to the reaction flask and placed into the glove box, with a clean, dry separatory funnel, and two clean, dry 150 mL Schlenk flasks. Solution was separated into an acetonitrile layer and hexanes layer. The light brown liquid products were characterized by ^{31}P NMR, but only the acetonitrile layer produced resonance (Fig. 15). ^{31}P NMR δ (ppm): -11.9 (t, J = 56 MHz), 20.4 (d, J = 56 MHz).

A 150 mL Schlenk flask was equipped with a small stir bar and methylenechloride (10 mL). Triethylamine (0.837 mL, 6.00 mmol) and methanesulfonic acid (0.195 mL, 3.00 mmol) were added in the glove box. The solution was stirred for 15 minutes. $[\text{PCl}_2\text{N}]_3$ (0.3493 g, 1.000 mmol) was added and the solution was stirred for 20 hours. The volatile components were removed on the Schlenk line. The brown, oily product was characterized by ^{31}P NMR

(Fig. 11). ^{31}P NMR δ (ppm): -11.4 (t, J = 55 MHz), -0.8 (t, J = 44 MHz), 20.9 (d, J = 57 MHz), 21.0 (d, J = 43 MHz).

A 150 mL Schlenk flask was equipped with a small stir bar and chloroform (10 mL). Methanesulfonic acid (0.146 mL, 2.25 mmol) and $[\text{PCl}_2\text{N}]_3$ (0.1747 g, 0.5000 mmol) were added in the glove box. The solution was stirred for 20 hours. The volatile components were removed on the Schlenk line. The brown, oily product was characterized by ^{31}P NMR (Fig. 12). ^{31}P NMR δ (ppm): -6.4 (s), 20.1 (s).

A 150 mL Schlenk flask was equipped with a small stir bar and methylenechloride (7 mL). Triethylamine (0.279 mL, 2.00 mmol) and $[\text{PCl}_2\text{N}]_3$ (0.3482 g, 1.000 mmol) were added in the glove box. The solution was stirred for 20 hours. The volatile components were removed on the Schlenk line. The brown, oily product was characterized by ^{31}P NMR (Fig. 13). ^{31}P NMR δ (ppm): 19.9 (s).

$[\text{PCl}_2\text{N}]_3$ (0.0864 g, 0.2350 mmol) was added to a sealable, air-free NMR tube in a nitrogen atmosphere inside glove bag. MeSO_3H (0.049 mL, 0.750 mmol) and Et_3N (0.209 mL, 1.50 mmol) were added to the tube and placed into liquid nitrogen to freeze and inhibit reaction. Tube was connected to high line and torch-sealed. Starting to thaw promptly prior to characterization. Characterization was run in 400 MHz NMR over a 24 hour period, from the initial run, then 10 hours, 12 hours, 13.5 hours, 19 hours, and 24 hours (Fig. 16, 17). ^{31}P NMR δ (ppm): (1) 19.5 (s). (2-6) -12.7 (t, J = 54 MHz), -2.5 (t, J = 41 MHz), 1.9 (t, J = 43 MHz), 19.4 (s), 19.8 (d, J = 44 MHz), 19.6 (d, J = 53 MHz), 19.9 (d, J = 40 MHz).

Reactions of $[\text{PCl}_2\text{N}]_3 + \text{DMF}$

$[\text{PCl}_2\text{N}]_3$ (0.1014 g, 0.275 mmol) was added to a clean 150 mL Schlenk flask. DMF (4 mL, 0.05 mol). The solution was stirred for 22 hours. The volatile components were removed on the Schlenk line. The brown, oily product was characterized by ^{31}P NMR (Fig. 19). ^{31}P NMR δ (ppm): -25.9 (t, J = 32 MHz), -13.8 (s), -12.6 (d, J = 32 MHz), -11.9 (d, J = 38 MHz), -11.2 (d, J = 34 MHz), -6.0 (s), 11.9 (s), 18.8 (t, J = 40 MHz), 22.0 (t, J = 35 MHz).

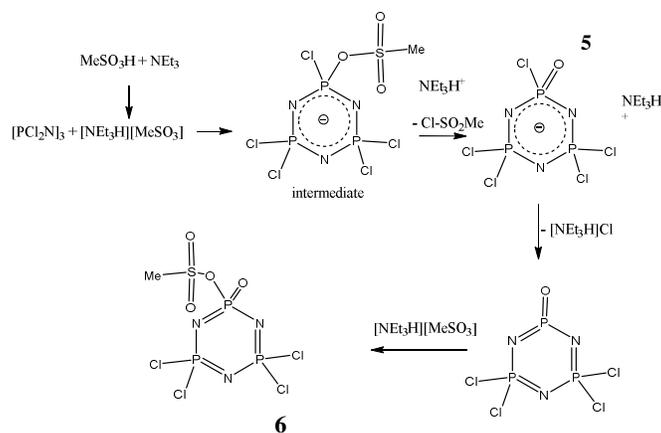
$[\text{PCl}_2\text{N}]_3$ (0.1039 g, 0.2826 mmol) was added to a 150 mL Schlenk flask equipped with a small stir bar and a condenser with a bubbler. DMF (4 mL, 0.05 mol) was added. The mixture was refluxed for 22 hours. The volatile components were removed on the Schlenk line. The black, viscous product was characterized by ^{31}P and ^1H NMR

(Fig. 20, 21). ^{31}P NMR δ (ppm): -20.5 (s) 400 MHz, -20.5 (s) 300 MHz. ^1H NMR δ (ppm): 2.50 (s), 2.72 (s), 2.81 (s), 3.09 (s), 3.28 (s), 8.98 (s), 9.34 (s), 9.74 (s).

iii. Results and Discussion

Chlorine/oxygen exchange reactions with MeSO_3^-

Initially, in the reactions of $[\text{PCl}_2\text{N}]_3$, NEt_3 and MeSO_3H the reactants were added simultaneously, and only starting materials were isolated (Fig. 4). When the methanesulfonic acid was deprotonated with the triethylamine base first and later reacted with $[\text{PCl}_2\text{N}]_3$, reaction took place as was observed by ^1H , ^{31}P NMR and ^{13}C spectroscopy (Fig. 5, 6, 7). The initial reactions were done in a 1:3:3 stoichiometric ratio of $[\text{PCl}_2\text{N}]_3$ to methanesulfonic acid to triethylamine. However, upon altering the ratio to 1:1:1 (Fig. 8), it was found that the stoichiometric properties of this reaction were of high importance, and greatly alter the ratio of species formed by ^{31}P NMR spectra. The examination of reactions in the 1:2:2 (Fig. 9), 1:6:6 (Fig. 10), 1:3:6 (Fig. 11) stoichiometries, the last of which was the ratio that most closely resembles that required for Zarei's proposed mechanism (Scheme 1), all provided largely different spectra by NMR spectroscopy. Two species were also found by NMR spectroscopy, which were determined based on coupling constants of the resonances. This led to the conclusion that coupling was occurring between the triplet and doublet resonances found at ~ -12 ppm and ~ 20 ppm, respectively, with the resonances at -2 ppm and 20 ppm (where there is a smaller doublet resonance hidden inside of a larger doublet resonance) that closely correspond to the resonances in Scheme 2, of doublet and triplet resonances at ~ 19 ppm (**3**), ~ -6 ppm (**3**) and ~ -11 ppm (**4**) in the unpublished work by Ben Thome and Johanna Beres. The similarities in these resonances lead to the conclusion that **5** elicited the 20 ppm and -2 ppm resonances, whereas **6** produced the other resonances at 20 ppm and -12 ppm. Reactions of the $[\text{PCl}_2\text{N}]_3$ with each reactant were done separately ($[\text{PCl}_2\text{N}]_3 + \text{Et}_3\text{N}$, $[\text{PCl}_2\text{N}]_3 + \text{MeSO}_3\text{H}$) as well in order to understand the small impurity peaks appearing at the baseline in the ^{31}P NMR (Figs. 12 and 13). Though the exact mechanisms are not known, in order to provide the compounds that represent these resonances, it is proposed from previous work by the Tessier group that an ionic species with a charged singly substituted ring and a charged triethylamine compound is an option, as well as a methanesulfonic adduct or a singly substituted oxygen atom onto the ring.



Scheme 3. Proposed mechanism of $\text{MeSO}_3\text{H} + \text{Et}_3\text{N} + [\text{PCl}_2\text{N}]_3$ reaction based on unpublished work by Ben Thome and Johanna Beres, and Zarei's mechanism.

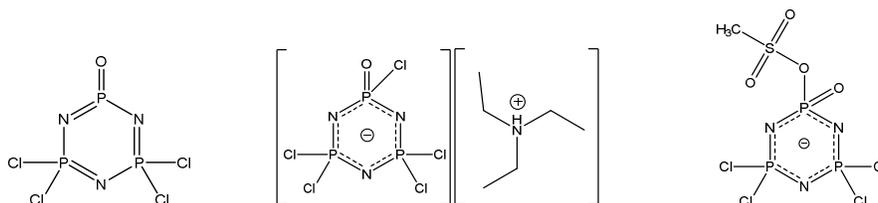


Fig.2 Possible substitution products by the reaction of compound **2** with methanesulfonic acid.

In order to decrease the yield of the initial species, separations using acetonitrile and hexanes were done on the product mixtures of the 1:3:3 and 1:6:6 reactions, due to the polarity of the acetonitrile and the non-polarity of the hexanes, causing immiscibility. It was thought that the proposed bi-product of this reaction is a salt ($\text{H}^+\text{NEt}_3\text{Cl}$) which would dissolve into the acetonitrile layer, whereas the phosphazene ring would be dissolved into the hexanes layer. However, this did not occur and all products found in the CH_3CN extract. The intermediary species greatly decreased, providing the spectrum in fig. 14, which can be compared to that in fig. 15, where the differences in species are apparent. However, the full substitution resulting in the $[\text{PON}]_3$ single molecule, **2**, would offer a single resonance through ^{31}P NMR spectroscopy due to the congruity of the phosphorus atoms in the molecule. Minor triplet resonances are found in each ^{31}P NMR of these reactions, that were present in the reaction of $[\text{PCl}_2\text{N}]_3$ with Et_3N , but not that of the reaction of $[\text{PCl}_2\text{N}]_3$ with MeSO_3H . These minor resonances were concluded to be substitution of the amine onto the phosphazene ring, and are not further discussed.

Due to the inability to obtain a single ^{31}P NMR resonance and thereby $[\text{PON}]_3$, the order of formation of the partially-substituted species was investigated. This called for an NMR test tube reaction. The reactants were added to an air-free, sealable NMR tube under a nitrogen atmosphere in a glove bag. The $[\text{PCl}_2\text{N}]_3$ was added first, followed by the MeSO_3H and Et_3N , and the tube was quickly frozen in a liquid nitrogen bath inside the glove bag in order to slow the reaction. When the reaction was ready to be started, the NMR tube was allowed to begin the thawing process which would cause the reaction to take place inside of the NMR instrument, as the formation of these species would be observed chronologically. This was done over a 24 hour period on a 400 MHz NMR spectrometer. These spectra were then overlaid as to easily see the differences of species growth as the reaction occurs (Figs. 16 and 17) demonstrating the proposed intermediate **3** product does indeed form first, as $[\text{PCl}_2\text{N}]_3$ resonance decreases (20 ppm) and that the final species **4** continues to grow. A fully substituted phosphonitrilic ring by oxygen atoms was not observed by any of the methanesulfonic acid and triethylamine reactions that were attempted, and therefore a new reactant was began to be used.

Chlorine/oxygen exchange reactions with dimethylformamide

After the initial attempts of full-substitution of the chlorine atoms with oxygen atoms using methanesulfonic acid and triethylamine resulted in only partial substitution, neat reactions with dimethylformamide (DMF) were done in similar air-free conditions, aiming for compound **1**. Chlorine/oxygen exchange has been reported by Marchetti,⁷ where molybdenum pentachloride reacts with carbonyl compounds like DMF (fig. 3) in chlorinated solvents in order to afford products with $\text{Mo}=\text{O}$ moieties. This reaction provided inspiration and characterizational data for the organic product derived from DMF. DMF was then used with $[\text{PCl}_2\text{N}]_3$, and this reaction under the right conditions was found to produce full substitution onto the phosphonitrilic ring, with a resonance at -20.54 ppm.

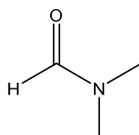
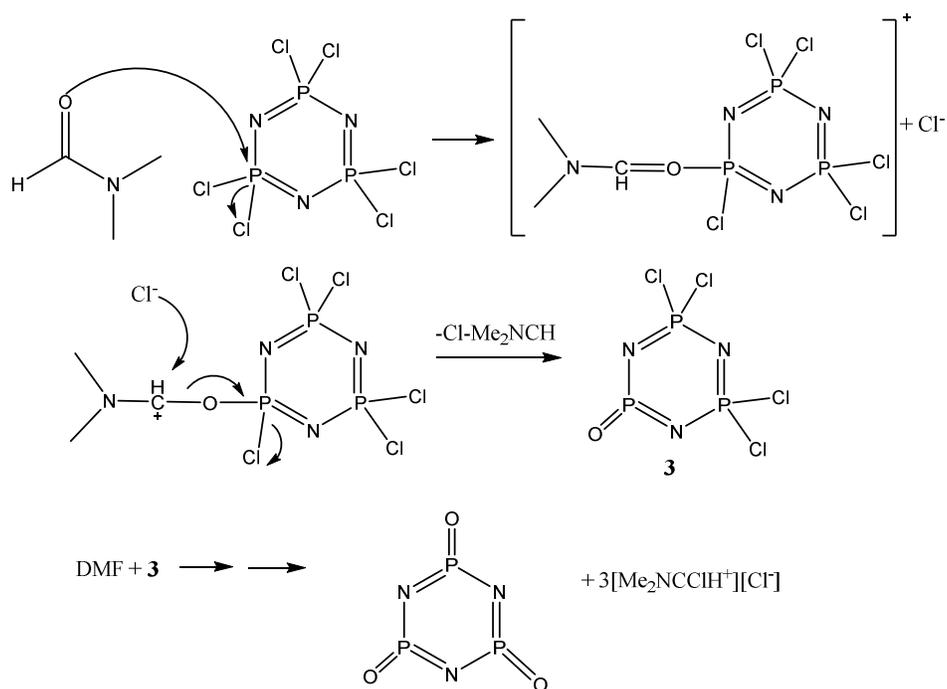


Fig. 3 Structure of dimethylformamide.

Reactions with DMF were done under neat, air-free conditions. After reaction for approximately 24 hours, crystals were isolated. Characterization initially was not possible of this crystal structure due to twinning and degradation of the crystal. Several other reactions of this kind were done in order to reproduce crystals that could be used for crystallographic characterization before their quick degradation period of a few days. When attempts of crystallization failed due to degradation in air or unwillingness of the product to crystallize by previously successful measures, ^{31}P NMR spectra were taken, showing multiple species, with singlets, doublets and triplets (Fig. 19), suggesting that chlorine/oxygen exchange was occurring, and further work-up was necessary.



Scheme 4. The proposed reaction mechanism of $[\text{PCl}_2\text{N}]_3$ and DMF, based on previous reactions done by Ben Thome and Johanna Beres.

Another reaction of $[\text{PCl}_2\text{N}]_3$ and DMF was refluxed. Prior to reflux, a yellow liquid was observed, but after, a viscous black-brown substance was present. Upon further examination, using ^{31}P NMR spectroscopy, the isolation of a singular, fully substituted system was concluded as the spectrum offered a single resonance at -20.54 ppm on the 400 MHz and 300 MHz NMR (Fig. 20). This was also characterized by ^1H NMR spectrum (Fig. 21), showing an downfield resonance at 8.5 ppm for the aldehyde proton, as well as two separate methyl resonances around 3 ppm, due to a partial resonant activity from the double bonded oxygen atom with the nitrogen atom.

iv. Conclusion

Reactions of $[\text{PCl}_2\text{N}]_3$, methanesulfonic acid and NEt_3 , though reactive, did not produce the proposed $[\text{PON}]_3$ single molecule. These reactions provided multiple species, presumably a mixture of **5** and **6**. Attempts to work-up the products to purity of a single species were unsuccessful. However, when reacting hexachlorocyclotriphosphazene with dimethylformamide, partial substitution with ^{31}P NMR resonances (ppm) at -25.9(t), -13.8(s), -12.6(d), -11.9(d), -11.2(d), -6.0(s), 11.9(s), 18.8(t), 22.0(t). The full substitution was found by ^{31}P NMR, providing a resonance at -20.5 ppm.

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Appendices

I. Safety Considerations

II. ^1H , ^{13}C and ^{31}P NMR spectra (Figs 4-21)

