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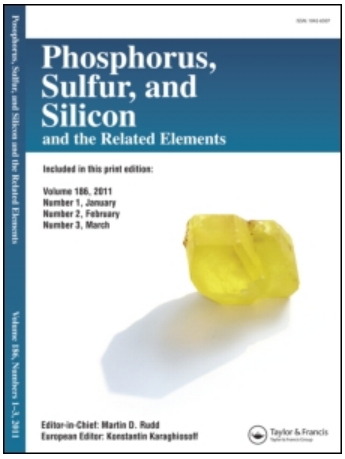

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ACID-BASE CHEMISTRY OF $[PCl_2N]_3$

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Online publication date: 12 August 2010

To cite this Article Heston, Amy J. , Panzner, Matthew , Youngs, Wiley J. and Tessier, Claire A.(2004) 'ACID-BASE CHEMISTRY OF $[PCl_2N]_3$', Phosphorus, Sulfur, and Silicon and the Related Elements, 179: 4, 831 — 837
To link to this Article: DOI: 10.1080/10426500490427277
URL: http://dx.doi.org/10.1080/10426500490427277

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Phosphorus, Sulfur, and Silicon, 179:831–837, 2004
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ISSN: 1042-6507 print / 1563-5325 online
DOI: 10.1080/10426500490427277

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ACID-BASE CHEMISTRY OF $[PCl_2N]_3$

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(Received August 21, 2003; accepted October 3, 2003)

An understanding of the chemistry of $[^{15}NPCl_2]_3$ is very important because this trimer is the major precursor to phosphazene polymers. In order to understand its sensitivity toward reaction conditions, $[^{15}NPCl_2]_3$ has been synthesized and characterized by modern spectral techniques. The goal of the study was to detect reactive impurities in the trimer, impurities that may account for the irreproducibility of the ring opening polymerization. Reactions of $[^{15}NPCl_2]_3$ with various acids and bases were conducted and the products have been characterized by multinuclear and variable temperature NMR spectroscopy and mass spectrometry. Particular attention was given to understanding the reactivity at the ^{15}N site toward acid and base reagents.

Keywords: Acid-base reactions; hexacyclocyclotriphosphazene

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The chloro phosphazene rings, especially $[PCl_2N]_3$, are important precursors to phosphazene polymers, by way of the polymer $[PCl_2N]_n$. Even though the ROP of $[PCl_2N]_3$ (or mixtures of $[PCl_2N]_3$ and larger rings) to $[PCl_2N]_n$ has been known for a long time, problems associated with the reproducibility of this process have never been fully solved.[1] As a first step toward solving such problems, we have decided to take a another look at the acid-base chemistry of the ring $[PCl_2N]_3$.

Though the substitution chemistry of $[PCl_2N]_3$ has been thoroughly examined,[2] acid-base chemistry has not been as well explored. Three general observations have been made with respect to acid-base chemistry.[3]

We thank our collaborators Prof. Peter Rinaldi and Debasish Banerjee for help with the NMR spectroscopy. We acknowledge support from the National Science Foundation.

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1. The nitrogen atoms of the ring $[PCl_2N]_3$ are poor Brönsted bases and the only adduct reported with a Brönsted acid is with the strong acid ($[PCl_2N]_3 \cdot HClO_4$).[4]
2. Only a few adducts of $[PCl_2N]_3$ with a Lewis acid have been isolated, $[PCl_2N]_3 \cdot AlBr_3$, $[PCl_2N]_3 \cdot (SO_3)_3$, and $[PCl_2N]_3 \cdot (AlCl_3)_2$.[5,6] The latter may be an ionic compound.[3]
3. N-methylimidazole and other strong amine bases bind to the phosphorus atoms of $[PCl_2N]_3$ to give complexes in which chloride has dissociated.[7]

This lack of information is surprising because the polymerization of $[PCl_2N]_3$ appears to involve acid-base chemistry. Depending on concentration, the ROP of $[PCl_2N]_3$ is accelerated or retarded by the Lewis acid PCl_5, a starting material of and, thereby, a frequent impurity in $[PCl_2N]_3$.[8] The BCl_3 and other Lewis acids lower the temperature of polymerization of $[PCl_2N]_3$ and formation of an adduct between BCl_3 and $[PCl_2N]_3$ has been proposed as the first step in this process.[1] HCl and H_2O both affect the polymerization, the latter possibly by converting the P—Cl bonds of $[PCl_2N]_3$ or PCl_5 to HCl.[8]

Herein we describe preliminary efforts to understand the acid-base chemistry involved in the ROP of $[PCl_2N]_3$ to $[PCl_2N]_n$. Most of the studies of the acid-base chemistry of $[PCl_2N]_3$ were done before the easy availability of modern NMR techniques so it would be useful to simply further characterize some of the compounds described above.

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EXPERIMENTAL

All reactions were conducted under argon or dinitrogen gas using standard Schlenk, glove bag, and glove box techniques. Solvents were distilled from drying agents before use. Glassware was oven dried at least 120°, assembled hot, and immediately subjected to vacuum. $[PCl_2N]_3$ and $AlBr_3$ were sublimed and stored under anaerobic conditions.

RESULTS AND DISCUSSION

The reaction of $AlBr_3$ with $[PCl_2N]_3$ in hexane resulted in precipitation of a white solid in good yield. The product is not the adduct $[PCl_2N]_3 \cdot AlBr_3$ but rather $[(PCl_2N)_3][HAlBr_4]$. The source of the proton is not known, though adventitious water would appear to be the most likely source. Note that no reaction took place between $[PCl_2N]_3$ and BCl_3, $B(C_6F_5)_3$ and $BF_3(OEt_2)$.

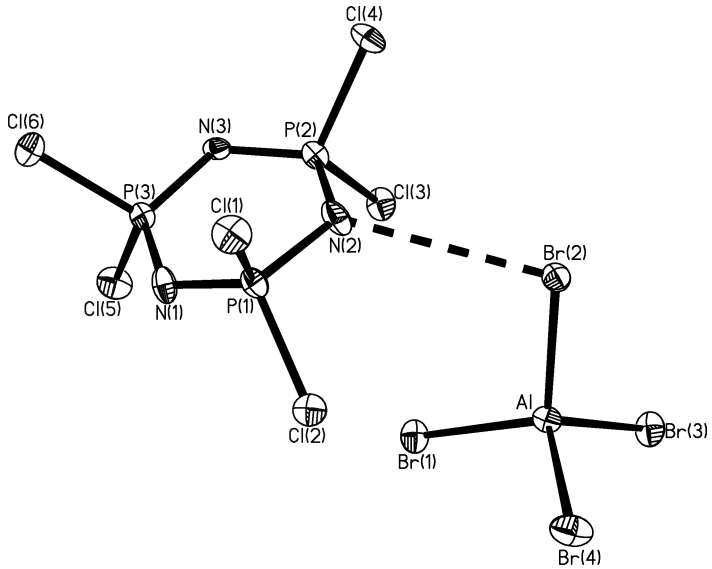

FIGURE 1 Crystal structure of $[(PCl_2N)_3][HAlBr_4]$.

As expected for the adduct $[PCl_2N]_3 \cdot AlBr_3$, the ^{31}P NMR spectrum showed the presence of two inequivalent phosphorus atoms at 19.6 and 27.0 ppm, shifted from the resonance of $[PCl_2N]_3$ at 20.5 ppm. However, the ^1H NMR spectrum showed a resonance at 10.2 ppm. This resonance is assigned to an N—H fragment and indicates that the ring is protonated.

The crystal structure of $[(PCl_2N)_3][HAlBr_4]$ ($R_1 = 4.21\%$) showed the presence of an $AlBr_4^-$ anion and a $[PCl_2N]_3$ ring, which, because of charge balance, would have to bear a positive charge. The hydrogen atom observed in the ^1H NMR spectrum was not directly observed in the crystal structure. Indirect evidence of the presence of a hydrogen atom at N(2) (see Figure 1) was provided by the N···Br distance and the distortions within the $[PCl_2N]_3$ ring. The N···Br distance of 3.36 Å is sufficiently long that it could be due to an N—H···Br hydrogen bond. The ring is slightly distorted from planarity. The two P—N bond distances to N(2) are consistent with single bonds (1.663(5) and1.663(5) Å) whereas the other four P—N distances show multiple bond character (1.553(5)–1.590(5) Å). These features are similar to those observed in the protonated ring $[P(N(i\text{-}Pr)H)_2N]_3[HCl]$, which contains an N—H···Cl hydrogen bond,[9] and comparisons are made in Figure 2.

Scheme 1 shows a possible mechanism for the formation of $[H(PCl_2N)_3]$-$[AlBr_4]$. In the first step, adventitious water, possibly water

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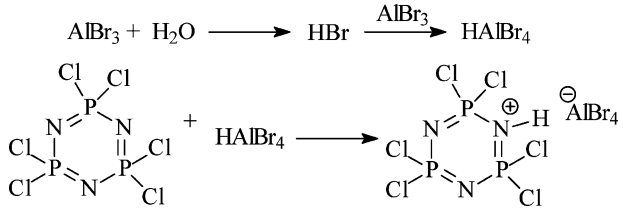

SCHEME 1

adsorbed on the halogenated reagents, reacts with $AlBr_3$ to form H-Br. HBr reacts with $AlBr_3$ to give the super acid $HAlBr_4$,[10] which then protonates the $[PCl_2N]_3$ ring. Note that the crystallographic data clearly indicate that only the $AlBr_4^-$ anion is present. Attempts to solve the crystal structure with Cl in place of some of the Br atoms did not give satisfactory results.

The isolation of $[H(PCl_2N)_3][AlBr_4]$ from the reaction of $AlBr_3$ and $[PCl_2N]_3$ indicated the presence of a protonic substance. Other unpublished work we have done and that of others[1] indicates the presence of protonic impurities, though we have never seen evidence of such an impurity in the sublimed $[PCl_2N]_3$ by NMR spectroscopy. In order to identify and isolate any proton source, the reaction of $[PCl_2N]_3$ and $(t\text{-Bu})N{=}P(N(CH_2)_4)_3$ in hexane was examined. The high Brönsted basicity and low nucleophilicity of $(t\text{-Bu})N{=}P(N(CH_2)_4)_3$[11] would deprotonate the protonic substance and give a salt that would be expected to be insoluble.

Treatment of $[PCl_2N]_3$ with $(t\text{-Bu})N{=}P(N(CH_2)_4)_3$ in hexane gives ~5% yield $[(PCl_2N)_2(POClN)][(t\text{-Bu})NH{-}P(N(CH_2)_4)_3]$, which slowly forms as a tan precipitate. This product can be rationalized as

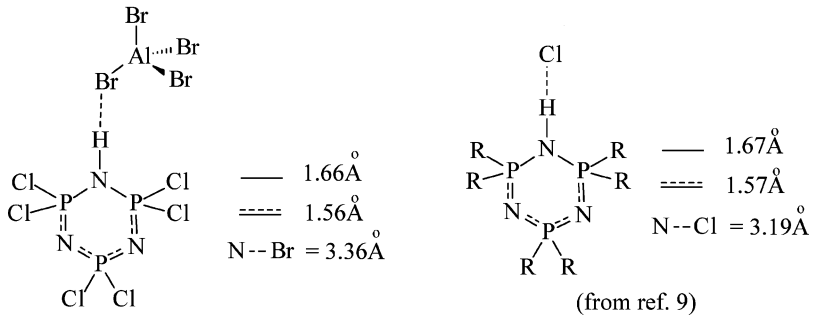

FIGURE 2 Structural comparisons between $[(PCl_2N)_3][HAlBr_4]$ and $[(P(N(i\text{-}Pr)H)_2N)_3][HCl]$ R=N(i-Pr)H.

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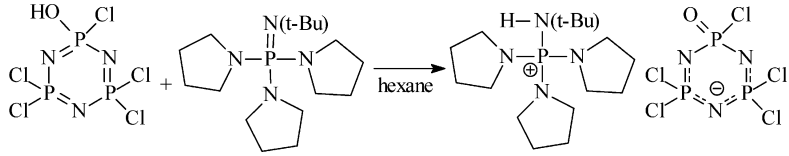
forming from the deprotonation of $[(PCl_2N)_2(P(OH)ClN)]$ by (t-Bu)-N=P$(N(CH_2)_4)_3$ (Eq. 1). The latter compound would be expected to be formed from the reaction of $[PCl_2N]_3$ and adventitious water.



(1)

Important spectral features of $[(PCl_2N)_2(POClN)][(t\text{-Bu})NH{-}P(N(CH_2)_4)_3]$ include a resonance at 7.76 in the ^1H NMR spectrum for the hydrogen atom bound to the nitrogen atom and three inequivalent phosphorus resonances (−4.4 (t), 20.9 (d), 22.7 (s)) in the ^{31}P NMR spectrum. In order to assure that correct spectral assignments had been made of the $[(t\text{-Bu})NH{-}P(N(CH_2)_4)_3^+]$ fragment, $[(t\text{-Bu})NH{-}P(N(CH_2)_4)_3]Cl$ was prepared by the reaction of gaseous HCl with (t-Bu)N=P$(N(CH_2)_4)_3$. $[(t\text{-Bu})NH{-}P(N(CH_2)_4)_3]Cl$ showed resonances at 7.96 ppm in the ^1H NMR spectrum for the hydrogen atom bound to the nitrogen atom and a resonance 22.8 ppm in the ^{31}P NMR spectrum.

The crystal structure of $[(PCl_2N)_2(POClN)][(t\text{-Bu})NH{-}P(N(CH_2)_4)_3]$ ($R_1 = 4.08\%$) showed a well-separated anion and cation. The $[(PCl_2N)_2(POClN)^-]$ ring was distorted with the POCl fragment bent out of the plane of the rest of the ring by 24° (Figure 3). The P—N distances to the POCl fragment were consistent with single bonds (1.625(3) and 1.626(3) Å) whereas the other P—N distances indicated multiple bonding character (1.552(3) – 1.593(3) Å). The P—N bonds in the $[(t\text{-Bu})NH{-}P(N(CH_2)_4)_3^+]$ cation were all consistent with single bonds (1.618(3)–1.631(3) Å). The hydrogen atom bound to the nitrogen atom was found.

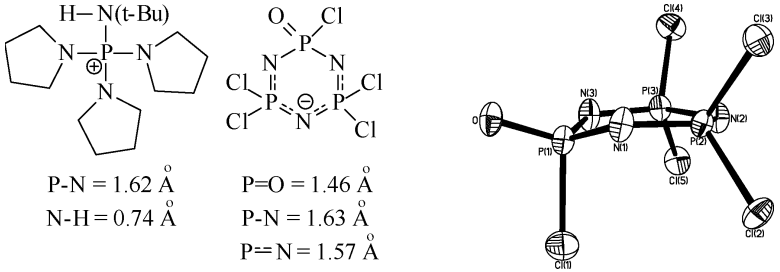


FIGURE 3 Crystal structure of $[(PCl_2N)_2(POClN)][(t\text{-Bu})NH{-}P(N(CH_2)_4)_3]$.

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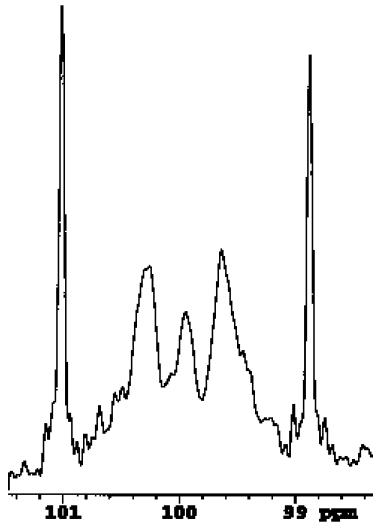

FIGURE 4 ^{15}N NMR spectrum of $[PCl_2{}^{15}N]_3$.

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To further study the ability of super acids to protonate the nitrogen atom of $[PCl_2N]_3$, the reaction of the commercially available super acid HOTf (triflic acid, $pK_a = -14$) with ^{15}N enriched (98%) $[PCl_2N]_3$ has been examined by NMR spectroscopy in C_6D_6. The ^{31}P resonance for $[PCl_2{}^{15}N]_3$ is split into a doublet of triplets due to coupling with the ^{15}N nuclei ($^1J(P{-}N) = 22$ Hz, $^3J(P{-}N) = 18$ Hz). Due to scalar relaxation of the second kind caused by the similar resonance frequencies of ^{15}N and ^{35}Cl, the ^{15}N NMR resonance of $[PCl_2\ {}^{15}N]_3$ shows broadening of the central peaks using a 300 MHz instrument (Figure 4). Evidence for protonation at a nitrogen atom in the reaction of $[PCl_2\ {}^{15}N]_3$ and HOTf include a broadened resonance at 12.8 ppm assigned to N–H in the ^1H NMR (proton of HOTf is observed at 11.1 ppm), an upfield shift by $\sim$11 ppm of the ^{15}N resonance and a 1 ppm upfield shift in the ^{31}P NMR resonance. The complex between $[PCl_2^{15}N]_3$ and HOTf decomposes after several days.

CONCLUSIONS

The reactions of $[PCl_2N]_3$ are far more sensitive to adventitious water than would be expected for a substance that appears to react only slowly with water in the solid state. No simple acid-base adducts between $[PCl_2N]_3$ and several group 13 Lewis acids were observed. The super acids $HAlBr_4$ and HOTf protonate the nitrogen atoms of $[PCl_2N]_3$.

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