Inorg. Chem. **2005**, *44*, 6518–6520

Inorganic Chemistry
Communication

Lewis Acid Adducts of $[PCl_2N]_3$

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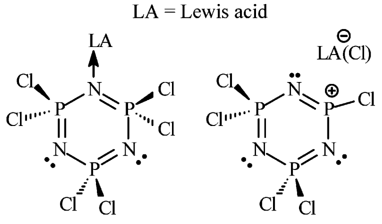
Received June 15, 2005

Reaction of aluminum trichloride or gallium trichloride with the extremely weak base hexachlorotriphosphazene gives adducts in which the group 13 element is bound to a phosphazene nitrogen atom. In solution, the adducts exhibit fluxional behavior. The phosphazene ring of the adducts is distorted into a slight chair conformation.

Phosphazene polymers have a tremendous variety of applications ranging from elastomers to anticancer drug delivery systems.[1] A major route to phosphazene polymers involves the ring-opening polymerization (ROP) of $[PCl_2N]_3$ to the polymer $[PCl_2N]_n$, which is then functionalized. The ROP is somewhat irreproducible. The two proposed mechanisms of the ROP involve acid−base chemistry, and Lewis acids such as BCl_3 and $AlCl_3$ catalyze the ROP.[1,2] A better understanding of the acid−base chemistry of $[PCl_2N]_3$ may provide insight into the irreproducibility of the ROP.

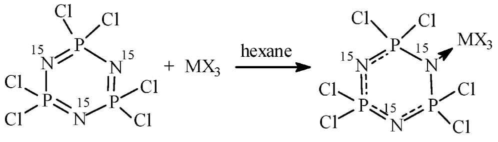
Though the nitrogen atoms of $[PCl_2N]_3$ are known to be weak bases,[3] the reactions of $[PCl_2N]_3$ with the Lewis acids $AlCl_3$ (1:2), $AlBr_3$ (1:1), SO_3 (1:3), $TaCl_5$ (1:1), $SbCl_5$ (1:1), and $VOCl_3$ (1:1) reportedly gave complexes of various stoichiometries.[3,4] (With $SbCl_5$ there is controversy that such chemistry takes place.) No ^{31}P NMR spectral or X-ray crystallographic data have been reported for the complexes. Two general structures have been proposed (Chart 1), a neutral adduct **1** or a phosphonium ion structure **2**. Structure **1** has been proposed as an intermediate in the BCl_3-catalyzed ROP of $[PCl_2N]_3$.[1,5] Structures of the type **2** have been proposed in the uncatalyzed ROP and the $AlCl_3$-catalyzed Friedel−Crafts substitution of $[PCl_2N]_3$.[3]

Chart 1



1 **2**

The reaction of $AlCl_3$ or $GaCl_3$ with $[PCl_2{}^{15}N]_3$ (97% ^{15}N) in hexane gave 1:1 complexes as colorless crystals (eq 1).



(1)

$MX_3 = AlCl_3$ or $GaCl_3$

We have been unable to isolate a 1:2 complex with $AlCl_3$, as had been previously reported.[4d] No isolable product was formed with BCl_3. Both $[PCl_2{}^{15}N]_3{\cdot}AlCl_3$ and $[PCl_2{}^{15}N]_3{\cdot}GaCl_3$ had melting points that were different from those of their respective reagents. The complexes were *highly water sensitive* and somewhat light sensitive in solution.

Thermal ellipsoid plots for the crystal structures of $[PCl_2{}^{15}N]_3{\cdot}AlCl_3$ and $[PCl_2{}^{15}N]_3{\cdot}GaCl_3$ are shown in Figures 1 and 2, respectively. The asymmetric unit of $[PCl_2{}^{15}N]_3{\cdot}AlCl_3$ contains half of two different molecules, whereas that of $[PCl_2{}^{15}N]_3{\cdot}GaCl_3$ contains two different molecules, the only statistically significant differences being in the dihedral angles of the nonplanar rings (see below).

Both complexes have the neutral adduct structure.[1] As expected from the difference in covalent radii of the group 13 atoms, the Al−N bonds (1.977(5) and 1.978(5) Å) are shorter than the Ga−N bonds (2.049(3) and 2.048(3) Å). The distances between the group 13 and the nitrogen atoms are in the range of dative bonds (M = Al, 1.94−2.10 Å[6];

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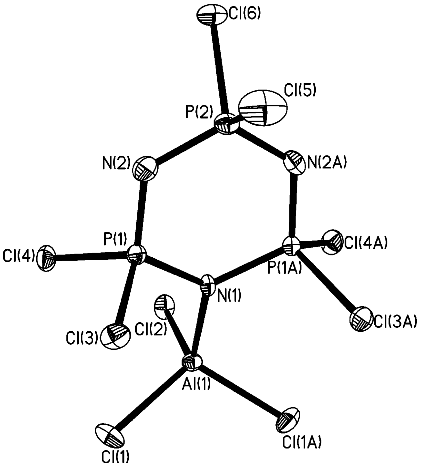

Figure 1. Thermal ellipsoid plot of one of the two molecules in the asymmetric unit of $[PCl_2{}^{15}N]_3 \cdot AlCl_3$.

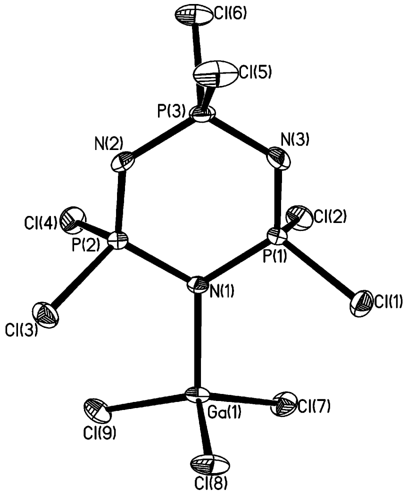

Figure 2. Thermal ellipsoid plot of one of the two moleules in the asymmetric unit of $[PCl_2{}^{15}N]_3 \cdot GaCl_3$.

M = Ga, 1.95−2.20 Å[7,8]). When compared to distances in other MCl_3 adducts of nitrogen-containing bases, the M−N bonds of both $[PCl_2{}^{15}N]_3 \cdot MCl_3$ (M = Al, Ga) are relatively long.

The phosphazene rings in the two $[PCl_2{}^{15}N]_3 \cdot MCl_3$ adducts are somewhat distorted from planarity to give chairlike structures in which the nitrogen atom bound to the group 13 element (N(1)) and the opposite phosphorus atom are below and above the plane of the remaining ring atoms (Figure 3). As indicated by dihedral angles, N(1) is bent away from this plane (M = Al, 19.7° and 17.7°; M = Ga, 20.6° and 20.5°) to a greater extent than the opposite phosphorus atom (M = Al, 11.7 and 3.8°; M = Ga, 7.8 and 7.3°). Because of the large difference of the latter dihedral angle for the two molecules of $[PCl_2{}^{15}N]_3 \cdot AlCl_3$, packing forces would appear to be patially responsible for this distortion. The P−N bonds that flank N(1) show single-bond character, both at 1.658(2) Å in $[PCl_2{}^{15}N]_3 \cdot AlCl_3$ and in the range 1.640(3)−1.648(3) Å with an average of 1.643(3) Å in $[PCl_2{}^{15}N]_3 \cdot GaCl_3$. The remaining P−N bonds show multiple-bond character ranging from 1.565(4)−1.572(4) Å (avg = 1.569 Å) for $[PCl_2{}^{15}N]_3 \cdot AlCl_3$ and 1.558(3)−1.578(3) Å (avg = 1.570 Å) for $[PCl_2{}^{15}N]_3 \cdot GaCl_3$ that are similar to those in $[PCl_2N]_3$.[9] Similar changes in ring geometry to those described above have been observed for adducts of more basic, trimeric, phosphazene rings,[10] most of which involve transition metals rather than main group metals.

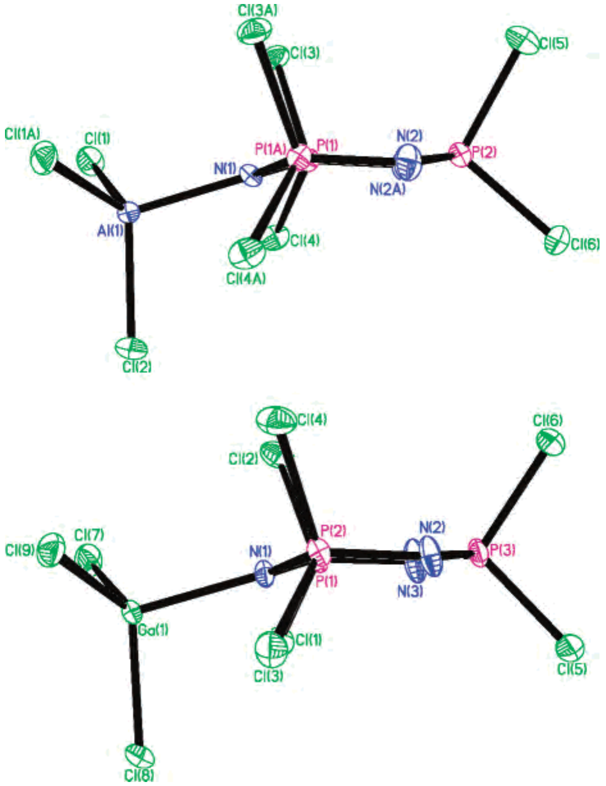

Figure 3. Chairlike structures of $[PCl_2{}^{15}N]_3 \cdot AlCl_3$ and $[PCl_2{}^{15}N]_3 \cdot GaCl_3$.

The NMR spectral data in C_6D_6 are consistent with fluxional structures in solution. The ^{31}P chemical shifts of the adducts differ only slightly from the resonance for $[PCl_2{}^{15}N]_3$ at 20.6 ppm.[11] The ^{31}P spectrum of $[PCl_2{}^{15}N]_3 \cdot GaCl_3$ showed two broad featureless signals at 23.4 and 23.3 ppm, the latter being a shoulder on the former. The two resonances are consistent with the formation of an adduct, but the broadness of the spectrum suggests that an exchange process is taking place, most likely dissociation and recombination of the adduct. The ^{31}P NMR spectrum of $[PCl_2{}^{15}N]_3 \cdot AlCl_3$ showed an even broader single resonance at 24.6 ppm, thereby suggesting that exchange is even more dominant in this adduct than in the gallium one. The resonances for the

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ring phosphorus atoms are also broad in the ^{31}P NMR spectrum of a carbaphosphazene adduct of $GaCl_3$.[7] The ^{15}N NMR spectra showed complex signals at 97.3 and 95.9 ppm for the $AlCl_3$ and $GaCl_3$ adducts, respectively, ~6 ppm upfield from the resonance of $[PCl_2{}^{15}N]_3$. The ^{27}Al NMR spectrum of $[PCl_2{}^{15}N]_3 \cdot AlCl_3$ showed a broad resonance at 107.1 ppm ($\lambda_{1/2} = 682$ Hz), which is shifted downfield ~7 ppm from the signal of $(AlCl_3)_2$ and is consistent with a four-coordinate aluminum center. Only at about −60°C or below are the adducts stable in solution, and this will be described in a later publication.

In summary, we have synthesized and characterized 1:1 adducts of $[PCl_2{}^{15}N]_3$ and the Lewis acids $AlCl_3$ and $GaCl_3$ in which the nitrogen atom of the ring serves as a weak base. We are studying the reactivity of $[PCl_2{}^{15}N]_3$ with other Lewis acids and with strong Brönsted acids.

Acknowledgment. This material is based upon work supported by the National Science Foundation under Grant No. CHE-0316944.

Supporting Information Available: Synthetic details and full crystallographic tables. This material is available free of charge via the Internet at http://pubs.acs.org.

IC050974Y