# Unusual Phosphoryl Donor Properties of $O{=}P(MeNCH_2CH_2)_3N$

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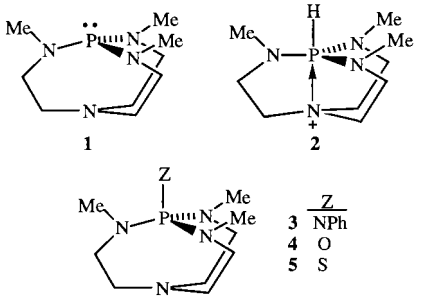
The title compound (**4**) in which transannular bridgehead−bridgehead bonding is absent, reacts with phosphoryl and silyl chlorides to give the isolable salts $[ZOP(MeNCH_2CH_2)_3N]Cl$ where Z = $Ph_2P(O)$, **6**(Cl); PhP(O)Cl, **7**(Cl); $^1/_2$PhP(O), **8**(Cl); $MeSiCl_2$, **14**(Cl); and $SiCl_3$, **15**(Cl). Spectroscopic evidence for $[ROP(MeNCH_2CH_2)_3N]^+$ cations, where R = H, **16**; Me, **17**; Et, **18**, and the isolation of the regioisomeric cations $[O{=}P(MeNCH_2CH_2)_3NR]^+$ (R = Me, **19**; Et, **20**; *n*-Pr, **21**; *n*-Bu, **22**) as their iodide salts is also reported. In the presence of $Cl_3PO$, $PCl_5$, or $SOCl_2$, **4** gives the $[ClP(MeNCH_2CH_2)_3N]^+$ cation (**26**) which is also formed when $P(MeNCH_2CH_2)_3N$ is oxidized with $C_2Cl_6$. The more sterically hindered analogue of **4**, namely $O{=}P(i\text{-}PrNCH_2CH_2)_3N$ (**28**) (whose synthesis is reported herein), reacts with MeI and EtI to afford the isolable salts $[O{=}P(i\text{-}PrNCH_2CH_2)_3NR]I$ [R = Me, **29**(I); Et, **30**(I)]. Cations **29** and **30** display $^1H$ and $^{13}C$ NMR spectra at room temperature that are consistent with a quaternization-induced rigidity of the cage that renders the $(CH_3)_2CH$ methyl groups inequivalent on the NMR time scale. Acyclic $O{=}P(NMe_2)_3$ reacts with $[R_3O]BF_4$ (R = Me, Et) giving the corresponding isolated salts $[MeOP(NMe_2)_3]BF_4$ and $[EtOP(NMe_2)_3]BF_4$. Reaction of HCl with $O{=}P(NMe_2)_3$ afforded sublimable $(Me_2N)_3P{=}O{\cdot}HCl$ which represents the first protonated phosphoryl species structured by X-ray crystallography. The transannular bond lengths in **6**(Cl) and **26**($PCl_6$) [1.948(5) Å and 1.934(8) Å, respectively] are within experimental error of the corresponding link in the $[HP(MeNCH_2CH_2)_3N]^+$ cation [1.967(8) Å].

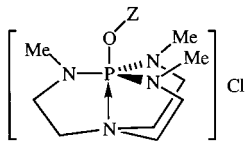
## Introduction

The proazaphosphatrane **1** has been shown to be a very strong nonionic base[1−3] that functions as a superior stoichiometric base in a variety of synthetically useful organic transformations,[4] as a superior catalyst for the efficient conversion of aryl isocyanates to isocyanurates[5] and for the protection of alcohols by acylation[6] and silylation.[7] Cation **2**, the protonated form of **1**, features a transannular P←N covalent bond [1.967(8) Å] that arises from upward pyramidalization of the bridgehead nitrogen in **1**.[8] We




have also found that **1** forms quasi-azaphosphatranes such as **3**−**5**,[9] in which the P−$N_{ax}$ bond distances (3.137 and 3.162 Å for **4**[10] and **5**,[11] respectively) are intermediate between the sum of the P and N van der Waals radii (3.35 Å) and the covalent transannular bond distance in **2**. Our studies of the catalytic properties of **1** and **3**−**5** revealed that bridgehead P−$N_{ax}$ transannulation plays a critical role in the catalytic transformation of isocyanates to isocyanurates using **1** or **3** and to carbodiimides using **4** or **5**.[5]

We report here our exploration of the role of transannulation in the basicity of the bridgehead nitrogen and the phosphoryl oxygen of **4** in the presence of various acceptors. Herein we describe the isolation of **6**(Cl)−**8**(Cl), **14**(Cl), and **15**(Cl) from




| Z | |
|---|---|
| **6** | $Ph_2P(O)$ |
| **7** | PhP(O)Cl |
| **8** | 1/2PhP(O) |
| **9** | $Cl_2P(O)$ |
| **10** | 1/2ClP(O) |
| **11** | 1/3P(O) |

| Z | |
|---|---|
| **12** | $Me_3Si$ |
| **13** | $Ph_3Si$ |
| **14** | $MeSiCl_2$ |
| **15** | $SiCl_3$ |

reactions of the corresponding Z chlorides with **4**; the spectroscopic evidence for salts **16**(Cl), **17**($BF_4$), and **18**($BF_4$) upon addition of HCl, $Me_3OBF_4$ and $Et_3OBF_4$ to **4**, respectively; and the isolation of salts **19**(I)-**22**(I) from the reaction of **4** with the corresponding alkyl iodides. For comparison, the acyclic analogue of **4**, namely $O{=}P(NMe_2)_3$ was allowed to react with $Ph_2P(O)Cl$, $PhP(O)Cl_2$, RI (R = Me, Et, *n*-Pr, *n*-Bu), HCl, $Me_3OBF_4$, and $Et_3OBF_4$. The last three reagents gave the salts **23**(Cl), **24**($BF_4$), and **25**($BF_4$), respectively. In the presence of

(1) Tang, J.-S.; Verkade, J. G. in "Synthetic Methods in Organometallic and Inorganic Chemistry", H. Karsch, Ed., **1996**, 3, 177.
(2) Laramay, M. A. H.; Verkade J. G. *Z. Anorg. Allg. Chem.* **1991**, *605*, 163.
(3) Laramay, M. A. H.; Verkade J. G. *J. Am. Chem. Soc.* **1990**, *112*, 9421.
(4) Mohan, T.; Arumugam, S.; Wang, T.; Jacobson, R. A.; Verkade, J. G. *Heteroatom Chem.* **1996**, *7*, 455.
(5) Tang, J.-S.; Mohan, T.; Verkade, J. G. *J. Org. Chem.* **1994**, *59*, 4931.
(6) D'Sa, Bosco A.; Verkade, J. G. *J. Org. Chem.* **1996**, *61*, 2963.
(7) D'Sa, B.; Verkade, J. G. *J. Am. Chem. Soc.* **1996**, *118*, 832.
(8) Lensink, C.; Xi, S. K.; Verkade J. G. *J. Am. Chem. Soc.* **1989**, *111*, 3478.
(9) Schmidt, H.; Lensink, C.; Xi, S. K.; Verkade, J. G. *Z. Anorg. Allg. Chem.* **1989**, *578*, 75.
(10) Tang, J.-S.; Dopke, J.; Verkade, J. G. *J. Am. Chem. Soc.* **1993**, *115*, 5015.
(11) Xi, S. K.; Schmidt, H.; Lensink, C.; Kim, S.; Wintergrass, D.; Daniels, L. M.; Jacobson, R. A.; Verkade, J. G. *Inorg, Chem.* **1990**, *29*, 2214.

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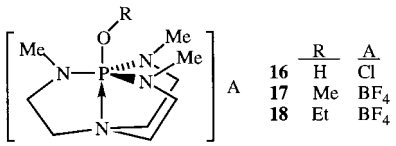
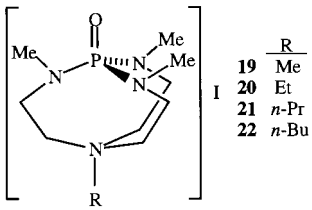


| | R | A |
|---|---|---|
| **16** | H | Cl |
| **17** | Me | $BF_4$ |
| **18** | Et | $BF_4$ |

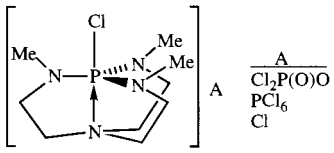


| | R |
|---|---|
| **19** | Me |
| **20** | Et |
| **21** | *n*-Pr |
| **22** | *n*-Bu |

$Cl_3PO$, **4** gives **26**[$Cl_2P(O)O$] and with $PCl_5$ or $Cl_2SO$, **4** affords **26**($PCl_6$) or **26**(Cl), respectively. Reaction of **1** with $C_2Cl_6$ also

[$(Me_2N)_3POR$]A

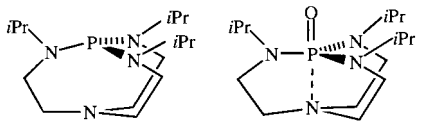
| | R | A |
|---|---|---|
| **23** | H | Cl |
| **24** | Me | $BF_4$ |
| **25** | Et | $BF_4$ |



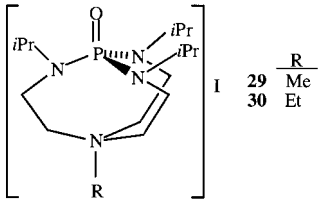
| A |
|---|
| $Cl_2P(O)O$ |
| $PCl_6$ |
| Cl |

**26**

gives cation **26** [as the chloride **26**(Cl)]. The reaction of **27**[11] with $Me_3SiOOSiMe_3$ gives **28** which also reacts with MeI and EtI, giving the salts **29**(I) and **30**(I), respectively. These



**27** **28**

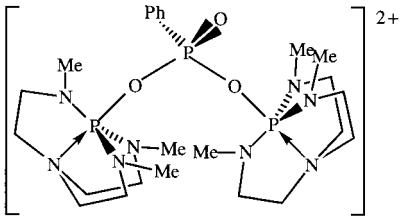


| | R |
|---|---|
| **29** | Me |
| **30** | Et |

compounds reveal the presence of inequivalent methyl groups in the *i*-Pr moieties on the NMR time scale, presumably owing to rigidity of the cage induced by quaternization of the bridgehead nitrogen. The structures of **6**(Cl) and **26**($PCl_6$), determined by X-ray means, feature unusually short transannular bond distances [1.948(5) and 1.934(8) Å, respectively]. We also report the isolation of **23**(Cl) which represents the first example of a fully characterized phosphoryl compound protonated on the phosphoryl oxygen. The structure of **23**(Cl) was verified by X-ray crystallography.

## Discussion

**Reactions.** Compound **6**(Cl) forms rapidly (<10 min) and quantitatively upon adding $Ph_2P(O)Cl$ to **4** at room temperature. In this reaction, the P atom in $Ph_2P(O)Cl$ apparently serves as an electrophilic site for attack by the nucleophilic oxygen of the P═O group. The formation of the stable cation **6** is favored by transannulation, resulting in a short $N_{ax}\rightarrow P$ coordinate bond (see later). Similarly, **4** reacts with one and 0.5 equiv of PhP(O)-$Cl_2$, giving **7**(Cl) and **8**(Cl), respectively, the cation in the latter possessing the structure depicted schematically.



**8**

Although **4** reacts with $Ph_2P(O)Cl$ and $PhP(O)Cl_2$, giving **6**−**8**(Cl), **4** in the presence of O═$PCl_3$ does not afford compounds **9**−**11**(Cl). Compound **4** in the presence of one equivalent of O═$PCl_3$ displayed two $^{31}P$ NMR peaks having the same intensity; that at −8.50 ppm corresponding to the dichlorophosphate anion $Cl_2PO_2^-$ and the other at −20.9 ppm associated with the chlorophosphonium cation **26**. Also present was a pair of doublets (−15.6 and −31.6 ppm, $^3J_{PP}$ = 68.0 Hz) of low intensity which decreased gradually as the former two peaks increased. The pair of doublets are indicative of a two-phosphorus system we tentatively assume is **9**(Cl) on the basis of mass spectral (ESI) evidence (*m*/*z* 350 for the cation). The formation of an analogous salt was observed previously as an intermediate in the reaction of O═$P(NMe_2)_3$ with $OPCl_3$.[12] These results are consistent with the reaction sequence in Scheme 1 in which the $Cl_2P$═O moiety (being more electronegative than the $Ph_2P$═O group in **6**(Cl)) weakens the $N_3P$−O bond sufficiently for the chloride anion to nucleophilically attack the phosphorus of the cage to form the tricyclic six-coordinate intermediate[13] shown, thus leading to **26**($Cl_2PO_2$). Apparently **9**(Cl) is more reactive than **6**[Cl] which can be isolated. Support for the formation of cation **9** stems from a mass spectrum (ESI) of the reaction mixture. In the positive mode, the spectrum displays a smaller peak for **9** (*m*/*z* 350) and a larger peak for **26** (*m*/*z* 251), while in the negative mode, a peak for the $Cl_2PO_2^-$ anion (*m*/*z* 134) is observed. The reaction of **4** and $PCl_5$ also gave **26**(Cl), and we assume O═$PCl_3$ was concomitantly formed since the $^{31}P$ chemical shift of O═$PCl_3$ (6.28 ppm) severely overlaps that of $PCl_5$ (6.50 ppm). When **4** was treated with excess $PCl_5$ at room temperature, bright green crystals were obtained which were shown by NMR and mass (ESI) spectroscopies and also by X-ray crystallography to be compound **26**($PCl_6$). The formation of **26**($PCl_6$) can be envisioned by either of the pathways suggested in Scheme 2. The production of O═$PCl_3$ in Scheme 2 was confirmed by monitoring the reaction in $CD_3CN$ and observing the intermediate appearance of $^{31}P$ signals at −20.3 ppm (**26**) and 6.65 ppm (O═$PCl_3$). Thus the reaction to form **26**(Cl) proceeds too quickly for the O═$PCl_3$ produced to react with **4** to form **26**($Cl_2PO_2$) in detectable amounts, since the peak at −9.0 ppm corresponding to the anion $Cl_2PO_2^-$ was not observed. Compound **26**(Cl) was also synthesized in quantitative yield in reactions 1 and 2.

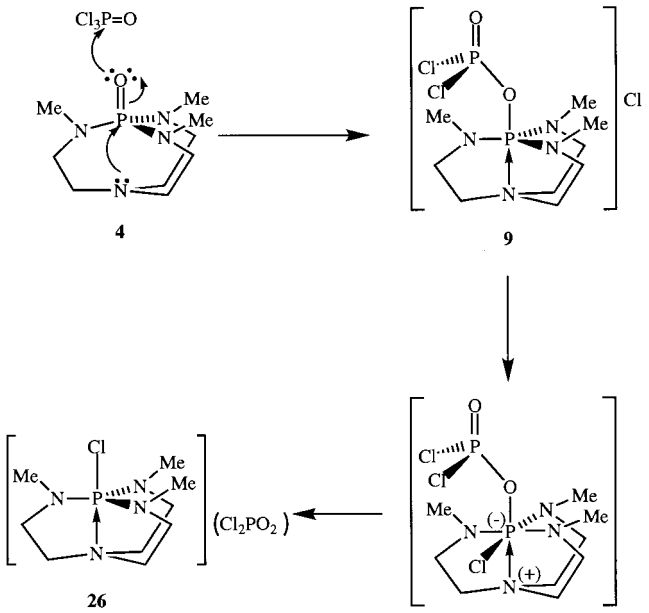
$$\mathbf{1} + Cl_3CCCl_3 \rightarrow \mathbf{26}(Cl) + Cl_2C{=}CCl_2 \qquad (1)$$

$$\mathbf{4} + Cl_2SO \rightarrow \mathbf{26}(Cl) + SO_2 \qquad (2)$$

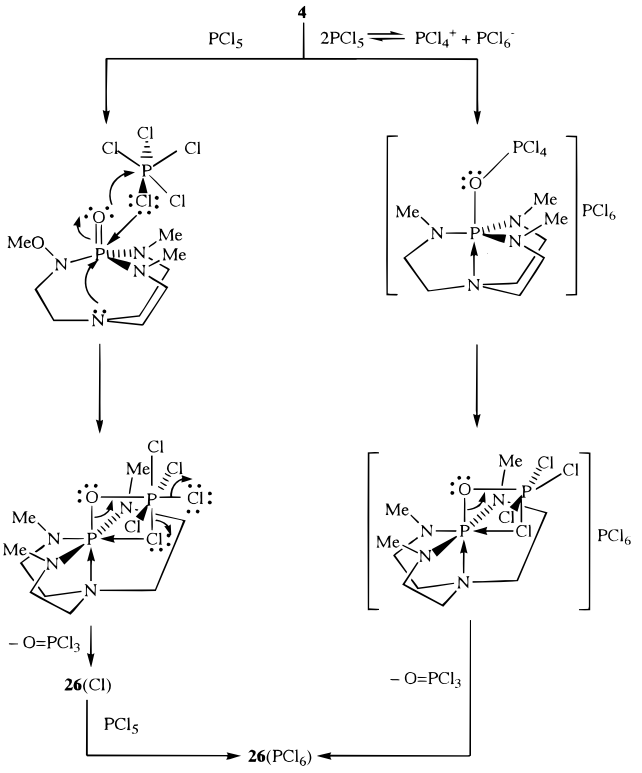
Compound **4** does not react with $Ph_2PCl$ [in contrast to $Ph_2P(O)Cl$] owing to the reduced electrophilicity of trivalent phosphorus in $Ph_2PCl$. The phosphorane $Ph_4PBr$ also fails to react with **4** perhaps mainly because of steric protection by the

(12) Dormoy, J. R.; Castro, B. *Tetrahedron Lett.* **1979**, *35*, 3321.
(13) Isolable polycyclic six-coordinate phosphorus compounds are well-known. See for example: (a) Luo, H.; McDonald, R.; Cavell, R. G. *Angew. Chem.* **1998**, *37*, 1098. (b) Ramirez, F.; Prasad, V. A. V.; Maracek, J. F. *J. Am. Chem. Soc.* **1974**, *96*, 7269.

**Scheme 1**

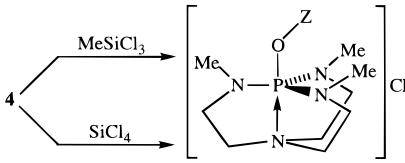


**Scheme 2**



phenyl groups and its reluctance to dissociate which could facilitate an $S_N1$ pathway. The importance of the stability afforded by transannulation in many of the above reactions is indicated by the failure of $(Me_2N)_3P{=}O$ to react with $Ph_2P(O)Cl$ (in contrast to **4**).

A $^{31}$P NMR spectrum of the reaction of **4** with one equivalent of $Me_3SiCl$ in $CD_3CN$ at room temperature revealed the presence of a broad signal at −1.1 ppm which moved upfield upon further addition of $Me_3SiCl$, suggestive of the formation of transannulated **12**(Cl). However, attempts to isolate a product by solvent evaporation, precipitation with $Et_2O$ or cooling to −30 °C, yielded only a mixture of starting material **4** [$^{31}$P NMR ($CD_3CN$) 22.4 ppm] and a product [$^{31}$P NMR ($CD_3CN$) 14.1 ppm] suspected to be **16**(Cl) (see later) that arose from partial hydrolysis of $Me_3SiCl$. A $^{31}$P VTNMR study in acetone-$d_6$ of a 1:1 mixture of **4** and the more electrophilic $Ph_3SiCl$ showed that the single resonance at 12.3 ppm at room temperature was split into two resonances upon lowering the temperature, so that at −60 °C the spectrum consisted of a large resonance at −23.9 ppm indicative of transannulated **13**(Cl) and a small peak at 22.4 ppm corresponding to starting material **4**. By reacting **4** with excess $MeSiCl_3$ and $SiCl_4$, **14**(Cl) and **15**(Cl) were isolated according to reactions 3 and 4, respectively. Attempts to grow



| | Z |
|---|---|
| **14**(Cl) | $MeSiCl_2$ |
| **15**(Cl) | $SiCl_3$ |

(3)

(4)

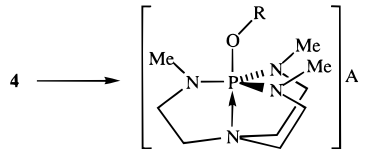
crystals of these compounds have not been successful. That cations **14** and **15** are transannulated, however, is strongly indicated by their upfield $^{31}$P chemical shifts (−30.0 and −35.0 ppm, respectively) which are substantially further upfield than that of untransannulated **4** (22.4 ppm) or, in fact, of the transannulated cation **2** (−11.0 ppm). Additional products of reactions 3 and 4 as well as reactions of **4** with other chlorosilanes will be reported in the due course.

In contrast to **5**, which undergoes alkylation at the bridgehead nitrogen or the sulfur atom with MeI and EtI, giving regioisomers,[14] **4** readily reacts with MeI in $CH_3CN$ to give only **19**(I) in quantitative yield at room temperature. Analogous reactions of **4** with EtI, *n*-PrI, and *n*-BuI in $CH_3CN$ were also carried out, giving **20**(I), **21**(I), and **22**(I), respectively. The constitutions of all these products were confirmed by NMR ($^1$H, $^{13}$C, $^{31}$P) and mass (ESI) spectroscopies. For these cations, confirmation of bridgehead nitrogen alkylation is afforded by their $^{31}$P chemical shifts, which do not differ substantially from that of **4**. The completion times and the temperatures for reactions of **4** with RI are 10 min (room temperature) for MeI; 24 h (50 °C) for EtI; 38 h (50 °C) for *n*-PrI; and 50 h (60 °C) for *n*-BuI, as monitored by $^{31}$P NMR spectroscopy. With *i*-PrI, PhI, or EtBr, no reaction was indicated by $^{31}$P NMR spectroscopy. The relative reaction rates in $CH_3CN$ of RI with **4**, namely, MeI > EtI > *n*-PrI > *n*-BuI ≫ *i*-PrI, PhI, EtBr, are consistent with $S_N2$ attack of the bridgehead nitrogen in **4** on the α carbon of RX. These results accord with the ideas that the bridgehead nitrogen is more nucleophilic than the O atom of **4** and that the bridgehead nitrogen in **4** is quite sensitive to the bulk of the alkylation agent.

For acyclic $O{=}P(NMe_2)_3$, which lacks a bridgehead nitrogen, attempts to alkylate the oxygen with RI (R = Me, Et, *n*-Pr, *n*-Bu) failed, giving only starting materials according to $^1$H and $^{31}$P NMR spectral monitoring of these reactions in $CD_3CN$. On the other hand, the protonation of the O atom of $O{=}P(NMe_2)_3$ with HCl, and analogously the alkylation of that atom with $Me_3OBF_4$ and $Et_3OBF_4$ occurs readily at room temperature to give **23**(Cl), **24**($BF_4$), and **25**($BF_4$), respectively, in quantitative isolated yields in less than 10 min. Interestingly the hydrochloride of $O{=}P(NMe_2)_3$ [**23**(Cl)] readily sublimes (very likely via HCl dissociation) without decomposition. The alkylation products are undoubtedly formed by an $S_N1$ mechanism in which a carbocation is attacked by a polar phosphoryl oxygen. As mentioned earlier, the phosphoryl bond in **4** is more nucleophilic than that in $O{=}P(NMe_2)_3$, thus favoring perhaps some $S_N1$

(14) Tang, J.-S.; Verkade, J. G. *J. Am. Chem. Soc.* **1993**, *115*, 1660.

alkylation of the O atom in this molecule. However, bridgehead N-alkylation could be a competing process. Indeed, the reaction mixture of **4** with $Et_3OBF_4$ showed two signals in $^{31}P$ NMR spectroscopy: 20.7 ppm corresponding to **20**($BF_4$) and −3.31 ppm, assumed to be **18**($BF_4$) based on its upfield $^{31}P$ chemical shift and on its $^1H$ NMR pattern (equation 5). The ratio of



| | R | A |
|---|---|---|
| **16** | H | Cl |
| **17** | Me | $BF_4$ |
| **18** | Et | $BF_4$ |

(5)

these two regioisomers is 2:1(**20**:**18**) based on $^{31}P$ NMR spectroscopy, suggesting that the bridgehead nitrogen is more nucleophilic than the phosphoryl oxygen in **4** despite the virtual planarity of its bridgehead nitrogen.[10] Similarly, the reaction of **4** with $Me_3OBF_4$ also gave signals at 20.5 ppm (**19**) and at −36.1 ppm (assumed to be **17**). However, **4** reacted with one equivalent of HCl giving one new signal at 14.6 ppm in the $^{31}P$ NMR spectrum which is assumed to be **16**. Although we were unable to isolate these regioisomers (**20**, **18**, and **17**, **19**) individually (owing mainly to their similar solubilities and tendency toward decomposition reactions) the NMR spectroscopic evidence for these regioisomers is strong.

**NMR Studies of Cations 19, 20, and 29.** Although the $^{31}P$ NMR spectrum of cation **19** shows one signal at 20.2 ppm its $^1H$ NMR spectrum revealed four broad triplets centered at 4.07, 3.70, 3.15, and 3.05 ppm for the bridge methylene groups. It was initially speculated that this observation was attributable to an unprecedented $^3J_{PH}$ of more than 300 Hz. However, its $^{31}P$-decoupled $^1H$ NMR spectrum showed a singlet at 2.65 ppm for the Me protons which appears as a doublet in the $^{31}P$-coupled $^1H$ NMR spectrum, and no change for the bridging methylene group resonances. Moreover, its $^{13}C$, $^1H$ NOESY NMR spectrum showed that the methylene group protons resonating at 4.07 and 3.15 ppm are attached to the same $N_{ax}CH_2$ carbon while the other two protons are attached to the same $MeNCH_2$ carbon. Thus, although the three bridging $MeNCH_2$ methylene carbons and the three bridging $N_{ax}(CH_2)_3$ carbons are equivalent by $^{13}C$ NMR spectroscopy, the two protons ($H_a$ and $H_b$) on any given bridging carbon are not equivalent and possess a substantial chemical shift difference (0.91 ppm). These observations are consistent with the following argument. While the cage structure of **4** is flexible with regard to ring inversion, rendering vicinal pairs of hydrogens equivalent, the bridgehead nitrogen in cation **19** donates its lone pair to an exocyclic methyl cation, giving rise to a considerably more rigid structure. As a consequence, there is expected to be a twist along the pseudo-3-fold axis of the cage that would account for the differentiation in the chemical environments of $H_a$ and $H_b$ on the methylene carbons of cation **19**.

The rigidity of the cage moiety of cation **19** imposed by the bridgehead alkyl group is sufficiently robust that it is preserved upon heating to 80 °C as shown in a VT $^1H$ NMR study. Moreover, when the bridging nitrogens bear *i*-Pr instead of Me groups as in cation **29**, two sets of doublets are observed for the $CH(CH_3)_2$ protons which are separated by about 0.06 ppm. This stereodifferentiating effect is also extended to the $CH_2$-$CH_3$ protons in cation **20** for which two sets of multiplets separated by about 0.09 ppm were observed.

**Structural Considerations.** The molecular structure drawing of **6**(Cl) in Figure 1 features a P−$N_{ax}$ distance of 1.948(5) Å (which is 40% shorter than the sum of the P and N van der Waals radii), a nearly tetrahedral bridgehead nitrogen and a

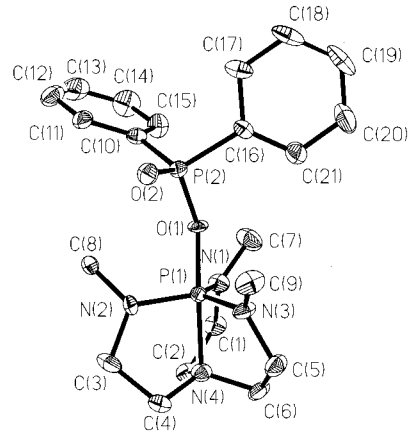



**Figure 1.** Molecular structure plot of the cation of **6**(Cl)·$CH_3CN$. Ellipsoids are drawn at the 50% probability level.

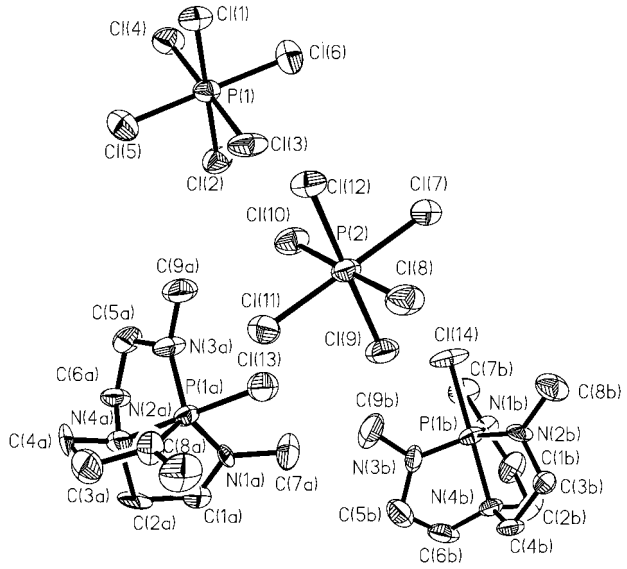



**Figure 2.** Molecular structure plot of **26**($PCl_6$). Ellipsoids are drawn at the 50% probability level.

nearly ideal trigonal bipyramidal phosphorus with $N_{eq}$−P−$N_{eq}$ angles of 119.4°. All these metrics are consistent with a fully transannulated structure. The structure of cation **6**, whose metrics are within experimental error of those of **2** [as judged by the 3 × (esd) criterion] is only the second structurally determined example of a fully transannulated phosphatrane. Upon transforming **4** to **6**(Cl), the P═O bond in **4** [1.473(2) Å[10]] lengthens to 1.667(4) Å in the P−O(O)$PPh_2$ linkage, which is longer than a normal single P−O bond (1.604 Å[15]). The long axial bonds, so typical of trigonal bipyramidal phosphorus compounds, can be interpreted in terms of a 3-center 4-electron MO system. Interestingly, the long $Ph_2P(O)O$−P distance in **6**(Cl) allows for a compensatory shortening of the $Ph_2P(O)$−OP distance to 1.581(4) Å, although this distance is (not unexpectedly) longer than the formal P═O linkage [1.471(4) Å] in this molecule. That the transannular P−N bond in cation **6** [1.948(5) Å] is longer than a normal single bond P−N link can be seen by comparing it to the P−$N_{eq}$ distances in this structure (average 1.654 Å).

The computer drawing of **26**($PCl_6$) in Figure 2, the third reported example of a fully transannulated phosphatrane, reveals a transannular distance of 1.934(8) Å and average $N_{eq}$−P−$N_{eq}$

(15) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*; John Wiley & Sons: New York, 1988.

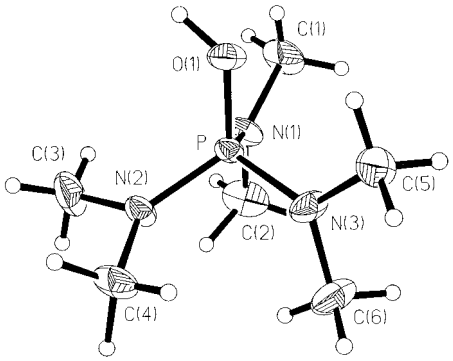
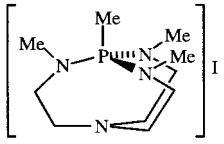
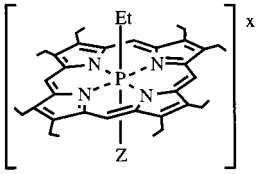



**Figure 3.** Molecular structure plot of the cation of **23**(Cl). Ellipsoids are drawn at the 50% probability level.

angles of 119.6°. Not unexpectedly the P−Cl distance in the cation [2.109(4) Å] is somewhat longer than that found in tetracovalent P−Cl compounds (2.00 Å[16]) and is almost within experimental error of those in its $PCl_6^-$ counterion [average 2.141(4) Å]. The transannular bond lengths in **6**(Cl), **26**(Cl), and cation **2** [1.948(5), 1.934(8), and 1.967(8) Å, respectively] are all within experimental error of one another as judged by the 3x(esd) criterion. We find it interesting that in view of the remarkable variability of these distances [from ca. 3.33 Å to 1.967(8) Å, depending upon the group bound to phosphorus in **1**[17]], each of the three rather different formally positive phosphorus substituents $H^+$, $Ph_2P(O)O^+$, and $Cl^+$ in cations **2**, **6**, and **26**, respectively, give rise to full transannulation in the cage structure of **1**. Equally interesting is our observation that the $CH_3^+$ substituent in **31**(I) does not induce transannulation [bridgehead−bridgehead distance, 2.773(2) Å].[4]




**31**




| | Z | x |
|---|---|---|
| **32** | =O··HOH | 0 |
| **33** | —OH | +1 |

The computer drawing of the cation **23**(Cl) in Figure 3 represents the first structure determination of a phosphoryl compound protonated on the phosphoryl oxygen. Interestingly the interatomic distance in the phosphoryl group [1.541(2) Å] is significantly longer than that observed in **4** [1.473(2) Å[10]] although it is not beyond the value quoted for a typical P═O bond (1.55 Å[15]). The P═O distance in **23**(Cl) is also considerably shorter than the $N_3P-O$ distances in **6**(Cl) [1.667(4) Å] wherein an $N_3PO-P(O)Ph_2$ covalent bond is formed. Somewhat unexpectedly, the O−H distance in **23**(Cl) [1.00(5) Å] is within experimental error of that in the water molecule ($R_e$ = 0.957 Å[18a]) suggesting the existence of a covalent single O−H bond in **23**(Cl). The $Cl^-$ ion in this compound is ∼1.83 Å from the hydrogen of this OH group and appears to be hydrogen-bound since the sum of the covalent and van der Waals radii are 1.28 and 2.95 Å, respectively.[18b] The Cl−H−O arrangement is nearly linear with an angle of 175°. The roughly $sp^2$ hybridization of the oxygen suggested by the P−O−H angle of 117.55(13)° is also consistent with the presence of a single OH bond even though the P═O linkage length is indicative of multiple bond character.[15] The structure of **23**(Cl) is interesting to compare with **32** in which the phosphoryl oxygen is hydrogen-bound to a water molecule.[19] The phosphoryl bond length [1.487(8) Å] in **32** is typical of a P═O link and the oxygen is 2.31 Å from the nearest hydrogen of the water. Also of interest is the structure of cation **33** which was derived from **32** by the addition of nonaqueous HCl.[19] Here the P−O bond length is typical of a single-bonded distance [1.635(5) Å[15]]. The O−H distance in **33** was not reported.

The P−N bond lengths in **23**(Cl) are normal (average 1.619 Å) and the nitrogen stereochemistries are uniformly almost planar (average sum of angles = 358.4°) which is quite typical of amino groups bound to third row elements. However, the geometry around phosphorus is inexplicably quite distorted from tetrahedral. Thus the N−P−N bond angles range from 104.95 to 117.55° and the O−P−N angles range from 103.52 to 117.48°. We are currently exploring the theoretical implications of these metrics.

## Experimental Section

Acetonitrile was dried with $CaH_2$, and $Et_2O$ was dried with sodium. All solvents were freshly distilled before use and all reactions were carried out under argon. $^1H$ and $^{13}C$ NMR spectra were recorded on a varian VXR-300 NMR spectrometer or a Bruker WM-200 NMR spectrometer. $^{31}P$ NMR spectra were recorded on a Bruker WM-200 NMR spectrometer using 85% $H_3PO_4$ as the external standard. High-resolution mass spectra were recorded on a KRATOS MS-50 spectrometer and ESI mass spectra were performed using a Finnigan TSQ700 spectrometer. Elemental analyses were performed in the Instrument Services Laboratory of the Chemistry Department at Iowa State University. X-ray data collections and structure solutions were conducted at the Iowa State Molecular Structure Laboratory. Refinement calculations were performed on a Digital Equipment Micro VAX 3100 computer using the SHELXTL-Plus[20] and SHELXL-93.[21,22]

Compounds **1**,[9] **4**,[9] and **22**[23] were synthesized according to our previously published methods. Compound **1** is commercially available from Strem Chemical Co. All other chemicals were purchased from Aldrich Chemical Co. and were used as received.

**$[Ph_2P(O)OP(MeNCH_2CH_2)_3N]Cl$, 6(Cl).** To a solution of **4** (0.175 g, 0.754 mmol) in 10 mL of $CH_3CN$ was added $Ph_2P(O)Cl$ (0.181 g, 0.760 mmol), and the resulting clear solution was stirred for 1 h at ambient temperature. After the volatiles were removed slowly under vacuum and the residue was washed with cold $Et_2O$ (2 × 5 mL), **6**(Cl) was obtained as colorless crystals (0.32 g, 90%). $^{31}P$ NMR ($CD_3CN$): $\delta$ 24.28 (d, $P_{tet}$, $^2J_{PP}$ = 49.2 Hz), −22.60 (d, $P_{tbp}$, $^2J_{PP}$ = 49.2 Hz). $^1H$ NMR ($CD_3CN$): $\delta$ 2.77 (d, 9H, $CH_3$, $^3J_{PH}$ = 12.0 Hz), 3.09 (dt, 6H, $N_{ax}CH_2$, $^4J_{PH}$ = 3.0 Hz, $^3J_{HH}$ = 6.0 Hz), 3.20 (dt, 6H, $N_{eq}CH_2$, $^3J_{PH}$ = 18.0 Hz, $^3J_{HH}$ = 6.0 Hz), 7.50−7.84 (m, 10H, Ph). $^{13}C$ NMR ($CD_3CN$): $\delta$ 38.58 (d, $CH_3$, $^2J_{PC}$ = 4.5 Hz), 46.87 (d, $N_{ax}CH_2$, $^3J_{PC}$ = 8.5 Hz), 47.15 (d, $N_{eq}CH_2$, $^2J_{PC}$ = 10.0 Hz), 129.87 (d, Ph, $^2J_{PC}$ = 13.5 Hz), 132.22 (d, Ph, $^3J_{PC}$ = 11.5 Hz), 133.44 (d, Ph, $^4J_{PC}$ = 3.0 Hz),

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134.06 (d, Ph, $^1J_{PC}$ = 141.5 Hz). MS (ESI) *m*/*z*: 433.2 (cation). Anal. Calcd for $C_{21}ClH_{31}N_4O_2P_2$: C, 53.79; H, 6.66; N, 11.95. Found: C, 53.42; H, 6.79; N, 11.64.

**[Ph(Cl)P(O)OP(MeNCH$_2$CH$_2$)$_3$N]Cl, 7(Cl).** To a solution of **4** (46.4 mg, 0.200 mmol) in 5 mL of $CH_3CN$ was added $PhP(O)Cl_2$ (60.0 mg, 0.300 mmol). After the resulting clear solution was stirred for 1 h at ambient temperature, **7**(Cl) was precipitated as a white solid (78 mg, 91%) by adding 5 mL of $Et_2O$ followed by washing with $Et_2O$ (2 × 5 mL). $^{31}$P NMR ($CD_3CN$): $\delta$ −31.51 (d, $P_{tbp}$, $^2J_{PP}$ = 60.0 Hz), 13.73 (d, $P_{tet}$, $^2J_{PP}$ = 60.0 Hz). $^1$H NMR ($CD_3CN$): $\delta$ 2.83 (d, 9H, $CH_3$, $^3J_{PH}$ = 12.0 Hz), 3.19−3.30 (m, 12H, $N_{ax}CH_2$ overlapped with $N_{eq}CH_2$), 7.57−7.97 (m, 5H, Ph). $^{13}$C NMR ($CD_3CN$): $\delta$ 38.38 (d, $CH_3$, $^2J_{PC}$ = 5.0 Hz), 46.14 (d, $N_{ax}CH_2$, $^3J_{PC}$ = 10.0 Hz), 46.55 (d, $N_{eq}CH_2$, $^2J_{PH}$ = 11.0 Hz), 130.30 (d, Ph, $^2J_{PC}$ = 18.0 Hz), 131.79 (d, Ph, $^3J_{PC}$ = 13.0 Hz), 134.91 (d, Ph, $^4J_{PC}$ = 3.0 Hz). (The signal of the *ipso* carbon in the Ph group was too weak to be observed.) MS (ESI) *m*/*z*: 391 (cation). Anal. Calcd for $C_{15}Cl_2H_{26}N_4O_2P_2$: C, 42.15; H, 6.09; N, 13.11; P, 14.52. Found: C, 41.77; H, 5.88; N, 13.34; P, 14.62.

**{PhP(O)[OP(MeNCH$_2$CH$_2$)$_3$N]$_2$}Cl$_2$, 8(Cl).** To a solution of **4** (0.130 g, 0.560 mmol) in 5 mL of $CH_3CN$ was added $PhP(O)Cl_2$ (50.0 mg, 0.256 mmol). The resulting clear solution was stirred for 1 h at ambient temperature. The product **8**(Cl) (0.15 g, 88%) was precipitated as a white solid by adding 5 mL of $Et_2O$ followed by washing with $Et_2O$ (2 × 5 mL). $^{31}$P NMR ($CD_3CN$): $\delta$ −11.08 (d, 2P, $P_{tbp}$, $^2J_{PP}$ = 42.4 Hz), −8.15 (t, 1P, $P_{tet}$, $^2J_{PP}$ = 42.4 Hz). $^1$H NMR ($CD_3CN$): $\delta$ 2.74 (d, 18H, $CH_3$, $^3J_{PH}$ = 12.0 Hz), 3.00 (t, 12H, $N_{ax}CH_2$, $^3J_{HH}$ = 6.0 Hz), 3.11 (dt, 12H, $N_{eq}CH_2$, $^3J_{PH}$ = 21.0 Hz, $^3J_{HH}$ = 6.0 Hz), 7.53−7.95 (m, 5H, Ph). $^{13}$C NMR ($CD_3CN$): $\delta$ 38.08 (d, $CH_3$, $^2J_{PC}$ = 3.0 Hz), 48.13 (d, $N_{ax}CH_2$, $^3J_{PC}$ = 7.5 Hz), 48.55 (d, $N_{eq}CH_2$, $^2J_{PC}$ = 8.3 Hz), 129.89 (d, Ph, $^2J_{PC}$ = 16.5 Hz), 132.96 (d, Ph, $^3J_{PC}$ = 11.3 Hz), 134.26 (d, Ph, $^4J_{PC}$ = 3.0 Hz). (The signal of the ipso carbon in the Ph group was too weak to be observed.) MS (FAB) *m*/*z*: 298 (cation $M^{2+}$/2). Anal. Calcd for $C_{24}H_{47}N_8P_3O_3Cl_2$: C, 43.71; H, 7.18; N, 16.99. Found: C, 43.21; H, 7.62; N, 16.51.

**[Cl$_2$MeSiOP(MeNCH$_2$CH$_2$)$_3$N]Cl, 14(Cl).** To a solution of **4** (92.8 mg, 0.400 mmol) in 5 mL of $CH_3CN$ was added excess $MeSiCl_3$ (90.0 mg, 0.600 mmol). The resulting clear solution was stirred for 1 h at room temperature, and then the volatiles were removed under vacuum. The residue was washed with $Et_2O$ (2 × 5 mL) to give **14**(Cl) as a white solid (0.11 g, 75%). $^{31}$P NMR ($CD_3CN$): $\delta$ −38.01. $^1$H NMR ($CD_3CN$): $\delta$ 1.02 (s, 3H, $SiCH_3$), 2.75 (d, 9H, $N_{eq}CH_3$, $^3J_{PH}$ = 13.4 Hz), 3.13−3.22 (m, 12H, $N_{ax}CH_2$ overlapping with $N_{eq}CH_2$). $^{13}$C NMR ($CD_3CN$): $\delta$ 5.93 (s, $SiCH_3$), 37.25 (d, $N_{eq}CH_3$, $^2J_{PC}$ = 5.0 Hz), 44.85 (d, $N_{ax}CH_2$, $^3J_{PC}$ = 9.4 Hz), 45.01 (d, $N_{eq}CH_2$, $^2J_{PC}$ = 10.9 Hz). MS (ESI) *m*/*z*: 346 (cation).

**[Cl$_3$SiOP(MeNCH$_2$CH$_2$)$_3$N]Cl, 15(Cl).** To a solution of **4** (92.8 mg, 0.40 mmol) in 5 mL of $CH_3CN$ was added excess $SiCl_4$ (102 mg, 0.60 mmol). The resulting clear solution was stirred for 1 h at ambient temperature and then all the volatiles were removed under vacuum. The residue was washed with $Et_2O$ (2 × 5 mL) to give **15**(Cl) as a white solid (0.12 g, 74%). $^{31}$P NMR ($CD_3CN$): $\delta$ −39.67. $^1$H NMR ($CD_3CN$): $\delta$ 2.78 (d, 9H, $N_{eq}CH_3$, $^3J_{PH}$ = 12.0 Hz), 3.19−3.29 (m, 12H, $N_{ax}CH_2$ overlapping with $N_{eq}CH_2$). $^{13}$C NMR ($CD_3CN$): $\delta$ 38.10 (d, $N_{eq}CH_3$, $^2J_{PC}$ = 5.5 Hz), 45.70 (d, $N_{ax}CH_2$, $^3J_{PC}$ = 6.5 Hz), 45.92 (d, $N_{eq}CH_2$, $^2J_{PC}$ = 8.0 Hz). MS (ESI) *m*/*z*: 367 (cation). Attempts to obtain consistent elemental analyses of this compound failed owing to its unusual sensitivity to moisture.

**[O=P(MeNCH$_2$CH$_2$)$_3$NMe]I, 19(I).** To a solution of **4** (92.8 mg, 0.400 mmol) in 5 mL of $CH_3CN$ was added excess MeI (0.170 g, 1.20 mmol). The resulting clear solution was stirred for 1 h at ambient temperature. Product **19**(I) was obtained as a white solid by precipitation with 5 mL of $Et_2O$ followed by washing with $Et_2O$ (2 × 5 mL). Recrystallization from $CH_3CN$ and $Et_2O$ (1:1) yielded **19**(I) as colorless crystals (0.12 g, 82%). $^{31}$P NMR ($CD_3CN$): $\delta$ 20.18. $^1$H NMR ($CD_3CN$): $\delta$ 2.67 (d, 9H, $N_{eq}CH_3$, $^3J_{PH}$ = 7.2 Hz), 2.97−3.25 (m, 6H, $N_{eq}CH_2$ overlapped with $N_{ax}CH_2$), 3.19 (s, 3H, $N_{ax}CH_3$), 3.70 (bdt, 3H, $N_{eq}CH_2$, $^3J_{HH}$ = 13.5 Hz), 4.09 (bdt, 3H, $N_{eq}CH_2$, $^3J_{HH}$ = 13.5 Hz). $^{13}$C NMR ($CD_3CN$): $\delta$ 34.74 (d, $N_{eq}CH_3$, $^2J_{PC}$ = 5.0 Hz), 48.37 (d, $N_{eq}CH_2$, $^2J_{PC}$ = 6.6 Hz), 64.24 (s, $N_{ax}CH_2$), 64.44 (s, $N_{ax}CH_3$). MS (ESI) *m*/*z*: 247 (cation). Anal. Calcd for $C_{10}H_{24}IN_4OP_2$: C, 32.10; H, 6.47; N, 14.97. Found: C, 31.62; H, 6.58; N, 14.86.

**[O=P(MeNCH$_2$CH$_2$)$_3$NEt]I, 20(I).** To a solution of **4** (92.8 mg, 0.400 mmol) in 5 mL of $CH_3CN$ was added excess EtI (0.180 g, 1.20 mmol). After the clear solution was stirred for 24 h at 60 °C, **20**(I) was precipitated as a white solid (0.11 g, 71%) by adding 5 mL of $Et_2O$ followed by washing with $Et_2O$ (2 × 5 mL). $^{31}$P NMR ($CD_3CN$): $\delta$ 20.25. $^1$H NMR ($CD_3CN$): $\delta$ 1.34 (t, 3H, $N_{ax}CH_2CH_3$, $^3J_{HH}$ = 7.2 Hz), 2.67 (d, 9H, $N_{eq}CH_3$, $^3J_{PH}$ = 7.5 Hz), 3.00−3.20 (m, 6H, $N_{ax}CH_2$ overlapped with $N_{eq}CH_2$), 3.38 and 3.48 (m, 2H, $N_{ax}CH_2CH_3$), 3.73 (bdt, 3H, $N_{eq}CH_2$, $^3J_{HH}$ = 13.5 Hz), 3.90 (t, 3H, $N_{ax}CH_2$, $^3J_{HH}$ = 13.5 Hz). $^{13}$C NMR ($CD_3CN$): $\delta$ 9.66 (s, $N_{ax}CH_2CH_3$), 34.79 (d, $N_{eq}CH_3$, $^2J_{PC}$ = 4.5 Hz), 48.25 (d, $N_{ax}CH_2$, $^3J_{PC}$ = 6.4 Hz), 61.00 (s, $N_{eq}CH_2$), 71.53 (s, $N_{ax}CH_2CH_3$). MS (ESI) *m*/*z*: 261 (cation).

**[HOP(NMe$_2$)$_3$]Cl, 23(Cl).** To a solution of $O=P(NMe_2)_3$ (0.900 g, 5.00 mmol) in 15 mL of THF was added excess HCl as a 1.0 M solution in $Et_2O$ (10.0 mL, 10.0 mmol). A white precipitate formed within one minute. The resulting reaction mixture was stirred for 1 h at ambient temperature after which additional **23**(Cl) was precipitated as a white solid (1.0 g, 95%) by adding 10 mL of $Et_2O$ followed by washing with $Et_2O$ (2 × 10 mL). Sublimation at 60 °C/1.0 Torr yielded **23**(Cl) (0.985 g, 91%) as colorless crystals. $^{31}$P NMR ($CD_3CN$): $\delta$ 33.54. $^1$H NMR ($CD_3CN$): $\delta$ 2.67 (d, 18H, $NCH_3$, $^3J_{PH}$ = 9.0 Hz). $^{13}$C NMR ($CD_3CN$): $\delta$ 36.93 (d, $NCH_3$, $^2J_{PC}$ = 5.3 Hz). MS (FAB) *m*/*z*: 180 (cation). Anal. Calcd for $C_6H_{19}ClN_3OP$: C, 33.42; H, 8.82; N, 19.49; P, 14.39; Cl, 16.45. Found: C, 33.22; H, 8.31; N, 19.44; P, 14.52; Cl, 16.25.

**[MeOP(NMe$_2$)$_3$]BF$_4$, 24(BF$_4$).** To a solution of $Me_3OBF_4$ (0.742 g, 5.00 mmol) in 10 mL of $CH_3CN$ was added $O=P(NMe_2)_3$ (0.950 g, 5.30 mmol). The resulting clear solution was stirred for 1 h at ambient temperature after which **24**($BF_4$) was obtained as a white solid (1.5 g, 90%) by precipitation with 10 mL of $Et_2O$ followed by washing with $Et_2O$ (2 × 10 mL). Recrystallization from $Et_2O$/$CH_3CN$ (1:1) at −20 °C gave **24**($BF_4$) (1.2 g, 73%) as colorless crystals. $^{31}$P NMR ($CD_3CN$): $\delta$ 39.45. $^1$H NMR ($CD_3CN$): $\delta$ 2.73 (d, 18H, $NCH_3$, $^3J_{PH}$ = 10.0 Hz), 3.85 (d, 3H, $CH_3$, $^3J_{PH}$ = 11.8 Hz). $^{13}$C NMR ($CD_3CN$): $\delta$ 37.20 (d, $NCH_3$, $^2J_{PC}$ = 4.6 Hz), 56.56 (d, $CH_3$, $^2J_{PC}$ = 7.1 Hz). MS (ESI) *m*/*z*: 194 (cation). Anal. Calcd for $BC_7F_4H_{21}N_3OP$: C, 29.92; H, 7.53; N, 14.95. Found: C, 29.80; H, 7.61; N, 14.84.

**[EtOP(NMe$_2$)$_3$]BF$_4$, 25(BF$_4$).** To a solution of $Et_3OBF_4$ (0.952 g, 5.00 mmol) in 10 mL of $CH_3CN$ was added $O=P(NMe_2)_3$ (0.950 g, 5.30 mmol). The resulting clear solution was stirred for 1 h at ambient temperature after which **25**($BF_4$) was obtained as a white solid (1.7 g, 91%) by precipitation with 10 mL of $Et_2O$ followed by washing with $Et_2O$ (2 × 10 mL). Recrystallization from $Et_2O$/$CH_3CN$ (1:1) at −20 °C gave **25**($BF_4$) (1.4 g, 75%) as colorless crystals. $^{31}$P NMR ($CD_3CN$): $\delta$ 37.58. $^1$H NMR ($CD_3CN$): $\delta$ 1.35 (td, 3H, $CH_2CH_3$, $^3J_{HH}$ = 9.6 Hz, $^4J_{PH}$ = 2.0 Hz), 2.73 (d, 18H, $NCH_3$, $^3J_{PH}$ = 13.6 Hz), 4.19 (dq, 2H, $CH_2CH_3$, $^3J_{PH}$ = 10.4 Hz, $^3J_{HH}$ = 9.6 Hz). $^{13}$C NMR ($CD_3CN$): $\delta$ 16.24 (d, $CH_2CH_3$, $^3J_{PC}$ = 7.8 Hz), 37.28 (d, $NCH_3$, $^2J_{PC}$ = 4.5 Hz), 66.81 (d, $CH_2CH_3$, $^2J_{PC}$ = 6.3 Hz). MS (FAB) *m*/*z*: 208 (cation). Anal. Calcd for $C_8H_{23}BF_4N_3OP$: C, 32.57; H, 7.86; N, 14.24. Found: C, 32.51; H, 7.89; N, 14.25.

**[ClP(MeNCH$_2$CH$_2$)$_3$N][O$_2$PCl$_2$], 26(O$_2$PCl$_2$).** To a solution of **4** (23.2 mg, 0.100 mmol) in 0.5 mL of $CH_3CN$ was added a solution of $OPCl_3$ (60.1 mg, 0.400 mmol) in 0.5 mL of $CH_3CN$. After the resulting solution was kept at room temperature for 2 h, all volatiles were removed under vacuum and the residue was washed with dry $Et_2O$ (2 × 0.5 mL), giving **26**($O_2PCl_2$) as a white solid (25 mg, 65%). $^{31}$P NMR ($CD_3CN$): $\delta$ −20.18 (cation), −8.52 (anion). $^1$H NMR ($CD_3CN$): $\delta$ 2.89 (d, 9H, $CH_3$, $^3J_{PH}$ = 15.0 Hz), 3.19 (m, 6H, $N_{ax}CH_2$), 3.31 (m, 6H, $N_{eq}CH_2$). $^{13}$C NMR ($CD_3CN$): $\delta$ 39.79 (d, $CH_3$, $^2J_{PC}$ = 5.0 Hz), 46.32 (d, $N_{ax}CH_2$, $^3J_{PC}$ = 9.0 Hz), 46.83 (d, $N_{eq}CH_2$, $^2J_{PC}$ = 9.0 Hz). MS (ESI) *m*/*z*: 251.5 (cation), 134 (anion).

**[ClP(MeNCH$_2$CH$_2$)$_3$N][PCl$_6$], 26(PCl$_6$).** To a solution of **4** (23.2 mg, 0.100 mmol) in 0.5 mL of $CH_3CN$ was added a solution of $PCl_5$ (84.1 mg, 0.400 mmol) in 0.5 mL of $CH_3CN$. The resulting solution was kept at 0 °C for 2 h, giving **26**($PCl_6$) as green yellow crystals (21 mg, 70%) after washing with cold $CH_3CN$ (2 × 0.5 mL). $^{31}$P, $^1$H, and $^{13}$C NMR data for the cation are identical to those of cation in **26**($O_2PCl_2$). MS (ESI) *m*/*z*: 251 (cation); 242 (anion).

**[ClP(MeNCH$_2$CH$_2$)$_3$N]Cl, 26(Cl). Method A.** To a solution of **1** (86.4 mg, 0.400 mmol) in 5 mL of $CH_3CN$ was added a solution of

$C_2Cl_6$ (97.2 mg, 0.410 mmol) in 3 mL of $CH_3CN$. After the resulting solution was stirred at room temperature for 2 h, all volatiles were removed under vacuum and the residue was washed with dry $Et_2O$ (2 × 5 mL), giving **26**(Cl) as a white solid in quantitative yield. The NMR and MS spectral data for the cation are identical to those of the cation in **26**($O_2PCl_2$).

**Method B.** To a solution of **4** (92.8 mg, 0.400 mmol) in 5 mL of $CH_3CN$ was added a solution of $Cl_2SO$ (52.5 mg, 0.420 mmol) in 3 mL of $CH_3CN$. The resulting solution was stirred at room temperature for 2 h. Then all the volatiles was removed in a vacuum and the residue was washed with dry $Et_2O$ (2 × 5 mL), giving **26**(Cl) as a white solid in quantitative yield. The NMR and MS spectral data are identical to those of cation in **26**($O_2PCl_2$). Anal. Calcd for $C_9H_{21}Cl_2N_4P$: C, 37.64; H, 7.37; N, 19.51. Found: C, 37.14; H, 7.92; N, 18.79.

**O=P(*i*-PrNCH$_2$CH$_2$)$_3$N, 28.** To a solution of **27** (0.900 g, 3.00 mmol) in 5 mL of $C_6H_6$ was added excess $Me_3SiOOSiMe_3$ (1.07 g, 6.00 mmol). The resulting clear solution was stirred at room temperature. After 48 h, all the volatiles were removed under vacuum giving a yellowish residue which upon recrystallization from $CH_3CN/Et_2O$ (1:1 v/v) yielded **28** as colorless crystals (0.61 g, 64%). $^{31}$P NMR ($CD_3CN$): $\delta$ 22.71. $^1$H NMR ($CD_3CN$): $\delta$ 1.10 (d, 18H, CH(C*H*$_3$)$_2$, $^4J_{HH}$ = 6.9 Hz), 2.62 (t, 6H, $N_{ax}CH_2$, $^3J_{HH}$ = 5.4 Hz), 2.89 (dt, 6H, $N_{eq}CH_2$, $^3J_{PH}$ = 14.1 Hz, $^3J_{HH}$ = 5.4 Hz), 3.64 (m, 3H, C*H*(CH$_3$)$_2$). $^{13}$C NMR ($CD_3CN$): $\delta$ 22.55 (d, CH(*C*H$_3$)$_2$, $^3J_{PC}$ = 2.6 Hz), 43.16 (d, $N_{eq}$-$CH_2$, $^2J_{PC}$ = 6.3 Hz), 47.97 (d, *C*H(CH$_3$)$_2$, $^2J_{PC}$ = 3.2 Hz), 54.9 (s, $N_{ax}CH_2$). HRMS *m*/*z* calcd for $C_{15}H_{33}N_4OP$: 316.23902. Found: 316.23891 (46.1, $M^+$). Anal. Calcd for $C_{15}H_{33}N_4OP$: C, 56.94; H, 10.51; N, 17.71. Found: C, 56.80; H, 10.75; N, 17.57.

**[O=P(*i*-PrNCH$_2$CH$_2$)$_3$NMe]I, 29(I).** To a solution of **28** (31.6 mg, 0.100 mmol) in 1 mL of $CH_3CN$ was added excess MeI (42.6 mg, 0.300 mmol). The resulting clear solution was stirred at room temperature for 24 h. The product **29**(I) was precipitated as a white solid (40 mg, 88%) by adding 1 mL of $Et_2O$ followed by washing with $Et_2O$ (2 × 1 mL). $^{31}$P NMR ($CD_3CN$): $\delta$ 20.16. $^1$H NMR ($CD_3CN$): $\delta$ 1.13 and 1.20 (d, 18H, CH(C*H*$_3$)$_2$, $^3J_{HH}$ = 6.0 Hz), 3.20 (s, 3H, $N_{ax}$-$CH_3$), 3.20−3.40 (m, 6H, $N_{ax}CH_2$ overlapped with $N_{eq}CH_2$), 3.60 (m, 3H, C*H*(CH$_3$)$_2$), 3.73 (bdt, 3H, $N_{eq}CH_2$, $^3J_{HH}$ = 12.0 Hz), 3.91 (t, 3H, $N_{ax}CH_2$, $^3J_{HH}$ = 12.0 Hz). $^{13}$C NMR ($CD_3CN$): $\delta$ 21.58 and 22.20 (s, CH(*C*H$_3$)$_2$), 41.41 (d, $N_{eq}CH_2$, $^2J_{PC}$ = 5.5 Hz), 48.56 (d, *C*H(CH$_3$)$_2$, $^2J_{PC}$ = 6.1 Hz), 64.29 (s, $N_{ax}CH_3$), 67.83 (s, $N_{ax}CH_2$). MS (ESI) *m*/*z*: 331 (cation).

**[O=P(*i*-PrNCH$_2$CH$_2$)$_3$NEt]I, 30(I).** To a solution of **28** (31.6 mg, 0.100 mmol) in 1 mL of $CH_3CN$ was added excess EtI (47.0 mg, 0.300 mmol). The resulting clear solution was stirred at 60 °C for 48 h. The product **30**(I) was precipitated as a white solid (41 mg, 87%) by adding 1 mL of $Et_2O$ followed by washing with $Et_2O$ (2 × 1 mL). $^{31}$P NMR ($CD_3CN$): $\delta$ 19.42. $^1$H NMR ($CD_3CN$): $\delta$ 1.12 and 1.18 (d, 18H, CH(C*H*$_3$)$_2$, $^3J_{HH}$ = 6.9 Hz), 1.32 (t, 3H, $CH_2CH_3$, $^3J_{HH}$ = 7.2 Hz), 3.20−3.40 (m, 6H, $N_{ax}CH_2$ overlapped with $N_{eq}CH_2$), 3.42 and 3.57 (s, 2H, $N_{ax}CH_2CH_3$), 3.57 (m, 3H, C*H*(CH$_3$)$_2$), 3.60−3.73 (m, 6H, $N_{ax}CH_2$ overlapped with $N_{eq}CH_2$). $^{13}$C NMR ($CD_3CN$): $\delta$ 9.59 (s, $N_{ax}CH_2CH_3$), 21.59 and 22.11 (s, CH(*C*H$_3$)$_2$), 41.33 (d, $N_{eq}CH_2$, $^2J_{PC}$ = 5.5 Hz), 48.61 (d, *C*H(CH$_3$)$_2$, $^2J_{PC}$ = 5.4 Hz), 64.43 (s, $N_{ax}CH_2$), 71.32 (s, $N_{ax}CH_2$-$CH_3$). MS (ESI) *m*/*z*: 345 (cation). Anal. Calcd for $C_{17}H_{38}IN_4OP$: C, 43.22; H, 8.11; N, 11.86. Found: C, 43.15; H, 8.28; N, 11.68.

**Attempted Reaction of 4 with Ph$_2$PCl.** To a solution of **4** (23.2 mg, 0.100 mmol) in 0.6 mL of $CH_3CN$ was added $Ph_2PCl$ (25.0 mg, 0.110 mmol). The resulting solution was kept at room temperature for 48 h or at 60 °C for 24 h, and then evaporated under vacuum to give only starting materials as shown by $^{31}$P and $^1$H NMR spectroscopies.

**Attempted Reaction of 4 with Ph$_4$PBr.** To a solution of **4** (23.2 mg, 0.100 mmol) in 0.5 mL of $CH_3CN$ was added a solution of $Ph_4PBr$ (46.2 mg, 0.110 mmol) in 0.5 mL of $CH_3CN$. The resulting solution was kept at room temperature for 48 h or at 60 °C for 24 h and then evaporated under vacuum to give only starting materials as shown by $^{31}$P and $^1$H NMR spectroscopies.

**Attempted Reaction of (Me$_2$N)$_3$P=O with Ph$_2$PCl.** To a solution of $(Me_2N)_3P$=O (18.0 mg, 0.100 mmol) in 0.6 mL of $CD_3CN$ was added $Ph_2PCl$ (25.0 mg, 0.110 mmol). The resulting solution was kept at room temperature for 48 h or at 60 °C for 24 h and then evaporated under vacuum to give only starting materials as shown by $^{31}$P and $^1$H NMR spectroscopies.

**Attempted Reaction of (Me$_2$N)$_3$P=O with Ph$_2$P(O)Cl.** To a solution of $(Me_2N)_3P$=O (18.0 mg, 0.100 mmol) in 0.6 mL of $CD_3CN$ was added $Ph_2P(O)Cl$ (26.4 mg, 0.110 mmol). The resulting solution was kept at room temperature for 48 h or at 60 °C for 24 h and then evaporated under vacuum to give only starting materials as shown by $^{31}$P and $^1$H NMR spectroscopies.

**Attempted Reaction of 4 with *i*-PrI.** To a solution of **4** (23.2 mg, 0.100 mmol) in 0.6 mL of $CH_3CN$ was added *i*-PrI (13.1 mg, 0.110 mmol). The resulting solution was kept at room temperature for 48 h or at 60 °C for 24 h, and then it was evaporated under vacuum to give only starting materials as shown by $^{31}$P and $^1$H NMR spectroscopies.

**Attempted Reaction of 4 with PhI.** To a solution of **4** (23.2 mg, 0.100 mmol) in 0.6 mL of $CH_3CN$ was added PhI (22.4 mg, 0.110 mmol). The resulting solution was kept at room temperature for 72 h or at 70 °C for 24 h, and then it was evaporated under vacuum to give only starting materials as shown by $^{31}$P and $^1$H NMR spectroscopies.

**Attempted Reaction of (Me$_2$N)$_3$P=O with RI (R = Me, Et, *n*-Pr, *i*-Pr).** To a solution of $(Me_2N)_3P$=O (18.0 mg, 0.100 mmol) in 0.6 mL of $CD_3CN$ was added excess RI (0.110 mmol). The resulting solution was kept at room temperature for 72 h in all cases and also at 60 °C for 24 h for EtI, *n*-PrI, and *i*-PrI. $^{31}$P and $^1$H NMR spectroscopies of all the reaction mixtures showed no evidence of reaction.

**Reaction of 4 with R$_3$OBF$_4$ (R = Me, Et) and HCl.** To a solution of **4** (23.2 mg, 0.100 mmol) in 0.6 mL of $CD_3CN$ was added 1 equiv of $R_3OBF_4$ or HCl. The resulting solution was kept at room temperature for 30 min, and then $^{31}$P NMR spectra were taken (see Discussion).

**General Procedure for NMR Reactions of 4 with Chlorosilanes.** To a solution of **4** (23.2 mg, 0.10 mmol) in 0.6 mL of $CD_3CN$ at 0 °C in an NMR tube was added the first portion of chlorosilane. After shaking the tube and then allowing it to stand at ambient temperature for 10 min, a $^{31}$P NMR spectrum was taken. The same procedure was followed after adding succeeding portions of chlorosilane. The $^{31}$P NMR chemical shifts (ppm) measured for various $Me_3SiCl$:**4** ratios in $CD_3CN$ were 22.4, 0:1; 14.5, 1:3; 2.3, 2:3; −1.1, 1:1; −1.9, 2:1; −2.0, 4:1; −2.1, 8:1; −2.2, 16:1. The $^{31}$P NMR chemical shifts (ppm) measured for various $Ph_3SiCl$:**4** ratios in $CD_3CN$ were 22.4, 0:1; 12.3, 1:1; 7.1, 2:1; 6.7, 3:1; 6.7, 4:1. When the $Ph_3SiCl$:**4** ratio exceeded 4:1, $Ph_3SiCl$ began to precipitate.

**VT NMR Study of 4 with Ph$_3$SiCl.** To a solution of **4** at 0 °C (23.2 mg, 0.100 mmol) in 0.6 mL of $CD_3CN$ in an NMR tube was added $Ph_3SiCl$ (29.5 mg, 0.100 mmol). After the tube was shaken and allowed to stand at room temperature for 10 min, $^{31}$P NMR spectra were taken at various temperatures. Before each measurement, the NMR tube was kept at a given temperature for 10 min. The $^{31}$P NMR chemical shifts (ppm) measured for this 1:1 mixture of $Ph_3SiCl$ and **4** were 12.3, 293 K; 3.8, 273 K; −0.6, 263 K; −5.2, 253 K; −9.4, 243 K; −13.2, 233 K; −16.9, 223 K; −20.7, 213 K; −23.9, 203 K.

**Crystal Structure Analysis of 6(Cl)·CH$_3$CN.** A colorless crystal of the title compound was mounted on a glass fiber on the Siemens P4RA for a data collection at 213(2) ± 1 K. The cell constants for the data collection were determined from reflections found from a 360° rotation photograph. Thirty five reflections in the range of 13.235−51.390° $\theta$ were used to determine precise cell constants. Pertinent data collection and reduction information is given in the Table 1. Lorentz and polarization corrections were applied and a nonlinear correction based on the decay in the standard reflections was applied to the data. A series of azimuthal reflections was collected for this specimen and a semiempirical absorption correction was applied to the data. The space group $P2_1/c$ was chosen based on systematic absences and intensity statistics. This assumption proved to be correct as determined by a successful direct-methods solution and subsequent refinement. All non-hydrogen atoms were placed directly from the *E* map and were refined with anisotropic displacement parameters. All hydrogens were treated as riding atoms with individual isotropic displacement parameters. Final refinements were then carried out.[20−22] A very disordered solvent molecule of acetonitrile was found in the asymmetric unit. The terminal carbon was modeled as having a split occupancy. Selected bond distances and angles are given in Table 2.

**Table 1.** Summary of Crystallographic Data for **6**(Cl)·$CH_3CN$, **26**($PCl_6$), and **23**(Cl)

| | **6**(Cl)·$CH_3CN$ | **26**($PCl_6$) | **23**(Cl) |
|---|---|---|---|
| empirical formula | $C_{21}H_{31}Cl_3N_4O_2P_2$, $C_2H_3N$ | $C_{18}H_{42}Cl_{14}N_8O_2P_4$ | $C_6H_{19}N_3OPCl$ |
| fw | 509.94 | 990.78 | 215.66 |
| space group | $P2_1/c$ | $P\bar{1}$ | $P2_1/n$ |
| $a$/Å | 7.996(2) | 7.584(2) | 8.267(2) |
| $b$/Å | 12.850(3) | 15.870(3) | 11.700(2) |
| $c$/Å | 24.906(5) | 16.278(3) | 12.216(2) |
| α/deg | 90 | 91.59(3) | 90 |
| $\beta$/deg | 90.93(3) | 90.81(3) | 107.63(3) |
| $\gamma$/deg | 90 | 91.57(3) | 90 |
| $V$/Å$^3$ | 2558.9(10) | 1957.4(7) | 1126.1(4) |
| $Z$ | 4 | 2 | 4 |
| $d$(calcd)/Mg·m$^{-3}$ | 1.324 | 1.681 | 1.272 |
| radiation ($\lambda$/Å) | Cu Kα (1.541 78) | Cu Kα (1.541 78) | Cu Kα (1.541 78) |
| temp/°C | −60 | −70 | −70 |
| diffractometer | Siemens P4RA | Siemens P4RA | Siemens P4RA |
| scan range ($2\theta$)/deg | 3.55−57.68 | 2.72−56.74 | 5.36−56.76 |
| scan method | $\theta-2\theta$ | $\omega$ | $\omega$ |
| abs coeff/mm$^{-1}$ | 2.745 | 10.821 | 4.083 |
| no. of reflcns collcd | 4457 | 6387 | 3191 |
| no. of indep reflcns | 3347 | 4979 | 1502 |
| R1 [$I \geq 2\sigma(I)$][a] | 0.0720 | 0.0420 | 0.0441 |
| wR2 [$I \geq 2\sigma(I)$][a] | 0.1863 | 0.2046 | 0.1104 |

**Table 2.** Selected Bond Length (Å) and Bond Angles (deg) for Compound **6**(Cl)·$CH_3CN$, **26**($PCl_6$), and **23**(Cl)

| | | | |
|---|---|---|---|
| | | **6**(Cl)·$CH_3CN$ | |
| P(1)−N(1) | 1.653(5) | P(1)−N(4) | 1.948(5) |
| P(1)−N(2) | 1.662(4) | P(1)−O(1) | 1.667(4) |
| P(1)−N(3) | 1.647(4) | P(2)−O(1) | 1.581(4) |
| N(1)−P−N(2) | 118.2(2) | C(2)−N(4)−C(4) | 112.7(4) |
| N(2)−P−N(3) | 119.3(2) | C(4)−N(1)−C(6) | 112.1(4) |
| N(1)−P−N(3) | 120.6(3) | C(2)−N(1)−C(6) | 113.3(4) |
| | | **26**($PCl_6$) | |
| P(1A)−N(1A) | 1.641(8) | P(1B)−N(1B) | 1.648(8) |
| P(1A)−N(2A) | 1.662(8) | P(1B)−N(2B) | 1.665(8) |
| P(1A)−N(3A) | 1.665(8) | P(1B)−N(3B) | 1.643(8) |
| P(1A)−N(4A) | 1.932(9) | P(1B)−N(4B) | 1.937(8) |
| P(1A)−Cl(13) | 2.112(4) | P(1B)−Cl(14) | 2.105(4) |
| P(1)−Cl | 2.137(4) (av) | P(2)−Cl | 2.147(4) (av) |
| N(1A)−P(1A)−N(2A) | 120.6(5) | N(1B)−P(1B)−N(2B) | 118.1(4) |
| N(2A)−P(1A)−N(3A) | 119.1(5) | N(2B)−P(1B)−N(3B) | 120.5(4) |
| N(1A)−P(1A)−N(3A) | 119.1(4) | N(1B)−P(1B)−N(3B) | 120.2(5) |
| C(2A)−N(4A)−C(4A) | 114.9(9) | C(2B)−N(4B)−C(4B) | 113.9(8) |
| C(4A)−N(4A)−C(6A) | 112.6(8) | C(4B)−N(4B)−C(6B) | 111.9(8) |
| C(6A)−N(4A)−C(2A) | 112.4(8) | C(6B)−N(4B)−C(2B) | 113.1(9) |
| | | **23**(Cl) | |
| P(1)−N(1) | 1.624(2) | P(1)−O(1) | 1.541(2) |
| P(1)−N(2) | 1.613(2) | H(1D)−O(1) | 1.00(5) |
| P(1)−N(3) | 1.619(2) | | |
| N(1)−P−N(2) | 104.95(13) | O(1)−P−N(1) | 107.29(12) |
| N(2)−P−N(3) | 106.67(13) | O(1)−P−N(2) | 117.48(12) |
| N(1)−P−N(3) | 117.55(13) | O(1)−P−N(3) | 103.52(12) |
| P−O(1)−H(1D) | 117(3) | | |

**Crystal Structure Analysis of 26($PCl_6$).** A crystal of **26**($PCl_6$) was mounted on a glass fiber on the Siemens P4RA for a data collection at 203(2) ± 1 K. The cell constants for the data collection were determined from reflections found from a 360° rotation photograph. Twenty six reflections in the range 25.844−44.742° $\theta$ were used to determine precise cell constants. Pertinent data collection and reduction information is given in the Table 1. Lorentz and polarization corrections were applied as was a nonlinear correction based on the decay in the standard reflections. A series of azimuthal reflections was collected for this specimen and a semiempirical absorption correction was applied to the data. The space group $P\bar{1}$ was chosen based on systematic absences and intensity statistics. This assumption proved to be correct as determined by a successful direct methods solution and subsequent refinement. All non-hydrogen atoms were placed directly from the $E$ map and were refined with anisotropic displacement parameters. All hydrogens were treated as riding-atoms with individual isotropic displacement parameters. Final refinements were then carried out.[20−22] Selected bond distances and angles are given in Table 2.

**Crystal Structure Analysis of 23(Cl).** A Crystal of **23**(Cl) was mounted on a glass fiber on the Siemens P4RA for a data collection at 203(2) ± 1 K. The cell constants for the data collection were determined from reflections found from a 360° rotation photograph. Twenty seven reflections in the range 16.992−37.483° $\theta$ were used to determine precise cell constants. Pertinent data collection and reduction information is given in the Table 1. Lorentz and polarization corrections were applied as was a nonlinear correction based on the decay in the standard reflections. A series of azimuthal reflections was collected for this specimen and a semiempirical absorption correction was applied to the data. The space group $P2_1/n$ was chosen based on systematic absences and intensity statistics. This assumption proved to be correct as determined by a successful direct methods solution and subsequent refinement. All non-hydrogen atoms were placed directly from the $E$

map and were refined with anisotropic displacement parameters. All hydrogens were refined with individual isotropic displacement parameters. The oxygen atom was found to be protonated with the hydrogen atom located 1.00 Å from the oxygen. Final refinements were then carried out.[20−22] Selected bond distances and angles are given in Table 2.

## Conclusions

Despite the thermodynamic stability of the P═O linkage in untransannulated **4**, the phosphoryl oxygen in this compound can be polarized and the P═O linkage can be lengthened by phenyl chlorophosphine oxides, forming isolable compounds such as **6**(Cl) in which transannulation has occurred to give a five-coordinate phosphorus geometry. The P═O bond in **4** is sufficiently polarized and weakened in the presence of $OPCl_3$ that it is cleaved forming **26**[$Cl_2P(O)O$] in which the cation is also fully transannulated. The sulfur reagent $SOCl_2$ also deoxygenates **4** to give cation **26**. The exocyclic lone pair on the pyramidal bridgehead nitrogen in **4** [average $C-N_{ax}-C$ angle = 119.9(2)°] is more nucleophilic than the phosphoryl oxygen, reacting with alkyl iodides to give cations **19**−**22** and **29**, **30** in which the cage moiety is structurally rigid. On the other hand, the phosphoryl oxygen competes for alkylation, forming transannulated cations **17** and **18** when carbocation sources of the type $[R_3O]BF_4$ are employed. It appears that a reliable indicator of transannulation in these phosphatranes is their chemical shift which ranges from ca. −11 to −41 ppm. This conclusion is substantiated by the observation that the substituents $H^+$, $Ph_2P(O)O^+$, and $Cl^+$ when attached to the phosphorus in **1** lead to a transannular distance of about 2.0 Å and $^{31}P$ chemical shifts in the aforementioned range.

Although $O{=}P(NMe_2)_3$, the acyclic analogue of **4**, appears to be too weak as a nucleophile to be phosphorylated or silylated, or to be alkylated by alkyl iodides, it does form cations **24** and **25** when the corresponding carbocation sources of the type $[R_3O]BF_4$ are employed. Both **4** and $O{=}P(NMe_2)_3$ can be protonated on the phosphoryl oxygen, and in the case of $O{=}P(NMe_2)_3$ this protonation site was verified by X-ray crystallographic analysis of its hydrochloride salt **23**(Cl). The preference of oxygen rather than nitrogen as the protonation site in **23**(Cl) parallels the same conclusion reached by others based on gas-phase ion cyclotron resonance mass spectroscopy studies of $O{=}P(NMe_2)_3$.[24]

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**Supporting Information Available:** Tables listing structure determination details, atomic coordinates, isotropic and anisotropic displacement parameters, bond lengths, and bond angles and figures showing structures of **6**(Cl), **26**($PCl_6$), and **23**(Cl) (57 pages). Ordering information is given on any current masthead page.

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