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# Conformational and Isomeric Preferences of Six-Membered Inorganic Heterocycles $[\mathrm{EtNP(E)(OR)}]_3$ (E = Lone Pair, O, S, or Se): A Synthetic, Spectroscopic, Structural, and Computational Study

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A silicophosphonate bearing four hydroxyl groups, $[\mathrm{RSi(OH)\{OP(O)(H)(OH)\}}]_2\mathrm{O}$ (**2**; R = $(2,6\text{-}{}^i\mathrm{Pr_2C_6H_3})\mathrm{N(SiMe_3)}$), has been isolated from the reaction between $\mathrm{RSi(OH)_3}$ and $[\mathrm{EtNPCl}]_3$. In contrast, the reaction between the sodium salt of substituted phenols and $[\mathrm{EtNPCl}]_3$ yields $[\mathrm{EtNP(OAr)}]_3$ [Ar = $-\mathrm{C_6H_3}{}^i\mathrm{Pr_2}$-2,6 (**3**), $-\mathrm{C_6H_2Me_3}$-2,4,6 (**4**), $-\mathrm{C_6H_3Me_2}$-2,6 (**5**), $-\mathrm{C_{10}H_7}$-1 (**6**), and $-\mathrm{C_6H_4}{}^t\mathrm{Bu}$-4 (**7**)]. The cis isomers **3a**−**7a** preferentially crystallize out from the cis/trans isomeric mixture. Single-crystal X-ray diffraction studies carried out for **3a**, **4a**, and **5a** reveal that the $\mathrm{P_3N_3}$ ring adopts a flattened-chair conformation with the aryloxy substituent on all three phosphorus atoms occupying the axial position. Oxidation of the cis isomers **3** and **5** by $\mathrm{H_2O_2}$, sulfur, and selenium yields the trichalcogenides $[\mathrm{EtNP(E)(OC_6H_3}{}^i\mathrm{Pr_2}\text{-}2,6)]_3$ (E = O (**8**), S (**10**), Se (**12**)) and $[\mathrm{EtNP(E)(OC_6H_3Me_2}\text{-}2,6)]_3$ (E = O (**9**), S (**11**), Se (**13**)). The reaction leading to the formation of the triselenide **12** also produces small quantities of the diselenide $[\mathrm{Et_3N_3P_3(OR)_3Se_2}]$ (R = $-\mathrm{C_6H_3}{}^i\mathrm{Pr_2}$-2,6) (**14**). The $\mathrm{P_3N_3}$ ring in these $\lambda^5$-phosphazanes is highly distorted and resembles more of a twist-boat conformation. The DFT calculations on model systems $[\mathrm{HNP(S)(OMe)}]_3$ (**15**) and $[\mathrm{HNP(Se)(OMe)}]_3$ (**16**) indicate five low-lying unique conformers **A**−**E**. The chair conformer with a triaxial-OMe group is identified as the lowest-energy conformer in both cases.

## Introduction

Among the main group E(III)−N imido systems,[1] the breadth of phosphorus−nitrogen chemistry is larger than that of nearly any other possible diatomic building block. Known P(III)−N compounds include a great variety of stable monomeric compounds apart from many types of cyclic and cagelike structures.[2−5] The presence of bulky substituents on phosphorus as well as on nitrogen has resulted in different effects, yielding large variations in the types of products formed.[3] For example, in the case of iminophosphine

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[RN=PCl], the compound exists as a monomer when the R group used is 2,4,6-$^t$BuC$_6$H$_3$.[4a] The same compound exists in the more well-known dimeric form when the substituent is changed to a 2,6-di-*iso*propylphenyl group.[4b,c] It appears that an appropriate selection of substituent can lead to the facile transformation between monomer, dimer, trimer, and other oligomers. The modification of the substituent on the phosphorus, rather than on nitrogen, also favors the formation of extremely crowded diazadiphosphetidines by the oxidative addition of tetrachloro-1,2-benzoquinone with aryloxy substituted $\lambda^3$-cyclotriphosphazane [EtNP(OR′)]$_3$ [R′ = −C$_6$H$_3$Me$_2$-2,6, −C$_6$H$_4$Br-4] (also known as triphosphatriazanes).[2d]

In an attempt to assess the extent of steric strain exerted by the phosphorus substituent in determining the conformation of six-membered rings; substituent disposition; and the possibility of ring contraction, expansion, or cleavage reactions, we have investigated in the present study the reaction of $\lambda^3$-[EtNPCl]$_3$ with a sterically encumbered silanetriol 2,6-$^i$Pr$_2$C$_6$H$_3$N(SiMe$_3$)Si(OH)$_3$ and the sodium salt of a series of *o*,*o*′-disubstituted phenols. The details of this study, reporting the formation of a molecular silicophosphonate and a series of tris-aryloxy-$\lambda^3$-cyclotriphosphazanes are presented herein.[6] The transformation of $\lambda^3$-cyclotriphosphazanes to their corresponding $\lambda^5$ counterparts by the action of H$_2$O$_2$, elemental sulfur, and elemental selenium is also described along with the X-ray crystal diffraction studies of the trisulfide and triselenide derivatives and computational studies on a series of model systems.

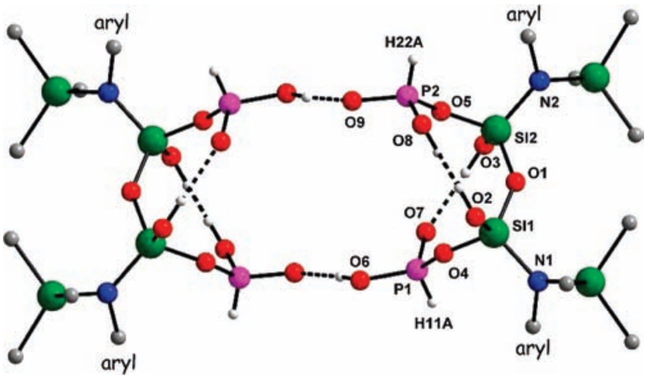
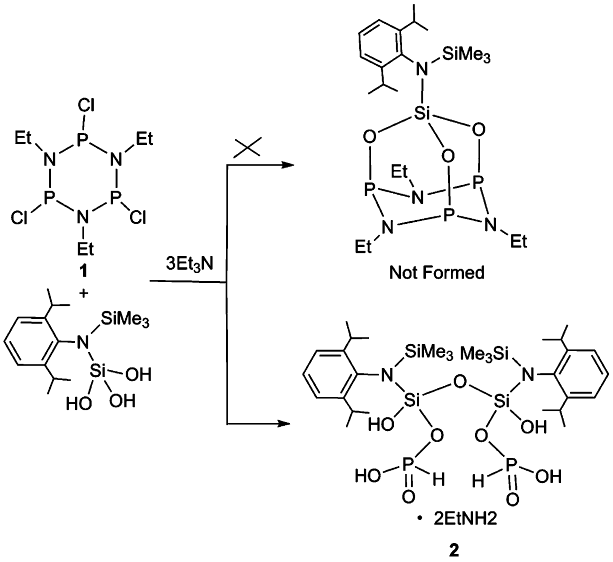


**Figure 1.** Dimeric structure in the crystal of **2** through O−H···O hydrogen bonds.

**Scheme 1.** Synthesis of Silicophosphonate **2**



## Results and Discussion

**A Molecular Silicophosphonate.** In an attempt to synthesize heteroadamantane containing Si, O, P, and N atoms from RSi(OH)$_3$[7] and [EtNPCl]$_3$[2] in the presence of Et$_3$N, an unusual molecular silicophosphonate [RSi(OH){OP(O)(H)(OH)}]$_2$O·2EtNH$_2$ (R = (2,6-$^i$Pr$_2$C$_6$H$_3$)NSiMe$_3$; **2**) is obtained in 35% yield (Scheme 1). The characteristic P−H stretching vibration in **2** is observed in the IR spectrum at 2407 cm$^{-1}$.[8] The resonance due to the P−H proton in the $^1$H NMR spectrum appears at $\delta$ 5.73 with a large $^1J_{PH}$ (670 Hz). Correspondingly, the proton-coupled $^{31}$P NMR spectrum shows a doublet centered at $\delta$ −9.4 ($^1J_{PH}$ = 670 Hz). The formation of **2** is consistent with the observation that the silanetriols undergo a facile self-condensation reaction[9] during the course of their reactions in the presence of acidic or basic impurities.[10] Water liberated during this step is consumed to hydrolyze $\lambda^3$-cyclotriphosphazane and eventually results in the formation of the final product. Compound **2** is built around a HO−P−O−Si(OH)−O−Si(OH)−O−P−OH inorganic backbone (Figure 1). Each of the phosphorus atoms has a (SiO)P(O)(H)(OH) local geometry, and hence each end of the molecule can be regarded as a monosilyl ester of H$_3$PO$_3$. The Ar(SiMe$_3$)N− groups account for the high solubility and kinetic stability of the heterocatenated inorganic chain in **2**. The Si−O−Si bond angle (142.2(5)°) is in very good agreement with the value obtained for [RSi(OH)$_2$]O (140.7(2)°).[9] The Si−OH groups form

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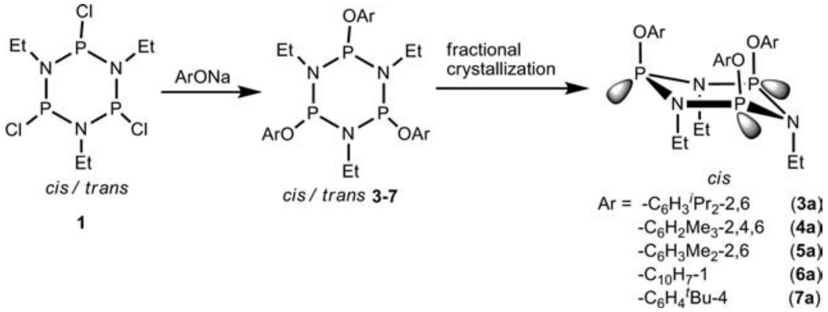
**Scheme 2.** Synthesis of **3**−**7**



intramolecular O−H···O hydrogen bonds[9] with the oxygen atom of the P═O and P−OH groups (Figure 1). Similarly, the P═O and P−OH groups of each phosphonate unit in the molecule form intermolecular O−H···O types of hydrogen bonds, and thus **2** exists as a dimer. While silanols containing three −OH groups on silicon and alkylphosphonic acids containing two −OH groups and a phosphoryl oxygen atom have recently been used for the synthesis of soluble molecular silicate and phosphate cages,[7,11] there are no known examples of compounds which simultaneously contain Si−OH and P−OH moieties along with a Si−O−P linkage, and hence the synthesis of **1** represents an important step in realizing SAPO types of silicate−phosphate hybrid materials.

**Synthesis and Spectral Characterization of Cyclotriphosphazanes $\lambda^3$-[EtNP(OR)]$_3$.** While the reaction of [EtNPCl]$_3$ with a kinetically stabilized bulky RSi(OH)$_3$ results in ring cleavage and the formation of a silicophosphonate **2**, it was reported more than a decade ago by Krishnamurthy and coworkers that the reaction of [EtNPCl]$_3$ with acidic hydrogen compounds such as phenols and alcohols proceeds neatly without any ring cleavage to form the corresponding aryloxy and alkoxy cyclotriphosphazanes.[2c,12] In light of the ring cleavage observed by us,[6] the ring contraction reported by Krishnamurthy and co-workers,[13] and the studies of Burford et al.,[4b,c] it was anticipated that replacing unsubstituted phenols with bulkier counterparts could have subtle consequences in ring cleavage, isomeric preferences, and ring conformations of cylcotriphosphazanes. Accordingly, in the present study, we have chosen to investigate the aryloxides of the cyclic system in detail by carrying out the reactions of [EtNPCl]$_3$ with phenols with bulky substituents. Thus, the reactions of [EtNPCl]$_3$ with the sodium salt of phenols such as $-OC_6H_3{}^iPr_2$-2,6, $-OC_6H_2Me_3$-2,4,6, $-OC_6H_3Me_2$-2,6, $-OC_{10}H_7$-1, and $-OC_6H_4{}^tBu$-4 have been carried out in a THF medium to isolate a mixture of cis and trans isomers of the correspondong aryloxides **3**−**7** (Scheme 2).

At the end of each reaction, a mixture of products, predominately containing the cis and trans isomers with variable amounts of oxidized products, has been obtained. Remarkably, the purification of this mixture by crystallization yields only the cis isomer as single crystals. While the cis products **3a**−**5a** and **7a** were obtained as single crystals from the isomeric mixture by a single crystallization, the 1-napthoxy derivative **6** was initially purified by silica gel column chromatography and then crystallized from acetonitrile to obtain pure cis isomer **6a**. It has been previously reported that it is possible to obtain the single crystals of both cis (chair-triaxial form) and trans (boat-triaxial form) isomers, successively, by fractional crystallization of the isomeric mixture in the case of less bulky simple aryloxides and alkoxides such as [EtNP(OR)]$_3$ (R = $C_6H_4$Br-4 and $CH_2CF_3$).[2c] However, in the present study, we obtained only the single crystals of the cis isomeric form. This result is contrary to the general expectation that one would actually expect the exclusive formation of the trans isomer, and not the cis isomer, in the case of the *o*,*o*′-disubstituted bulky aryloxides based on the earlier report that the 2,6-dimethylphenoxy derivative is obtained as only the trans isomer.[2c] Although surprising, the preferential formation of the cis isomer in the present case can be due to certain electronic requirements which override the steric bulkiness caused by the aryloxide groups on the same side of the $P_3N_3$ ring (vide infra).

Compounds **3a**−**7a** were found to be stable under an inert atmosphere for extended periods of time. Compounds **3a**−**5a** are stable even in the air for sufficiently longer periods of time, probably due to the steric protection around phosphorus by the ortho substituents of the aryloxide ligand. The stability of **6a** can again be attributed to the rather too bulky nature of the 1-napthoxy group. The presence of a $^t$Bu group on the para position, in compound **7a**, makes this compound the least stable among the series of compounds synthesized. Attempts to synthesize a $\lambda^3$-cyclotriphosphazane with 2,6-di-*tert*-butyl-4-methyl phenol did not yield the trisubstituted product. The product mixture contained several products which could not be separated. Similar problems were also observed in the attempted synthesis of pentafluorophenoxy derivative $\lambda^3$-[EtNP(OC$_6$F$_5$)]$_3$.

Compounds **3a**−**7a** have been characterized with the aid of elemental analysis, EI-MS, IR, and NMR ($^1$H and $^{31}$P) spectroscopic studies (Table S1, Supporting Information). All compounds yielded good analytical data. The M$^+$ ions could be detected in each case in the EI-MS (70 eV). The parent ion (M$^+$) is observed for each compound with lower intensities (2% for **3a**, 4% for **4a**, 2% for **5a**, and 2% for

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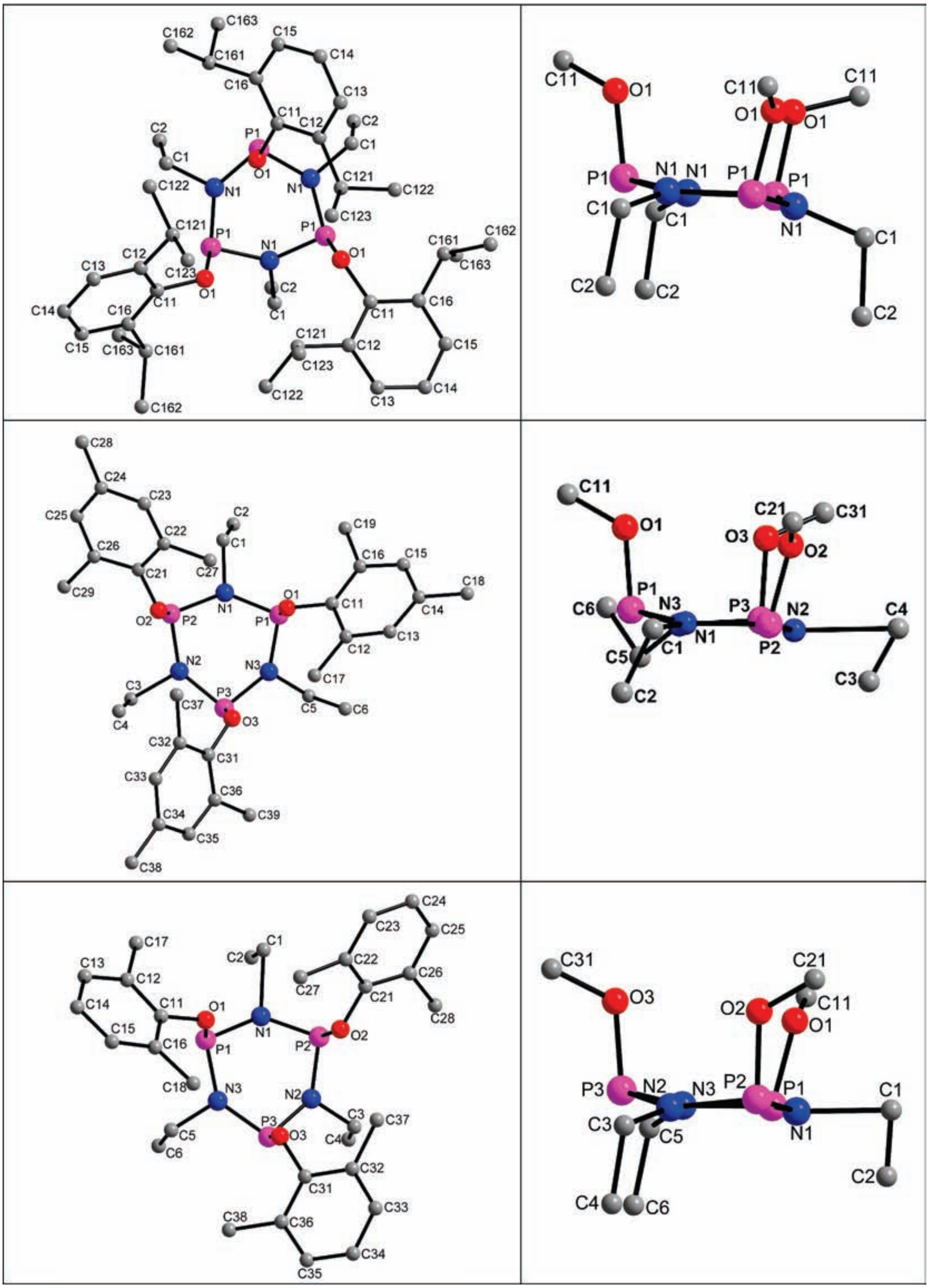

**Figure 2.** Molecular structure of (left, top to bottom) *cis*-[EtNP(OC$_6$H$_3{}^i$Pr$_2$-2,6)]$_3$ (**3a**), *cis*-[EtNP(OC$_6$H$_2$Me$_3$-2,4,6)]$_3$ (**4a**), and *cis*-[EtNP(OC$_6$H$_3$Me$_2$-2,6)]$_3$ (**5a**). P$_3$N$_3$ ring conformations are depicted on the right.

**6a**). Only one set of resonances was observed in the $^1$H NMR spectra of the pure cis isomers **3a**−**7a** for the −NEt and aryloxide groups. In the $^{31}$P NMR spectrum, **3a**−**7a** resonate as a sharp singlet in the range of $\delta$ 90−100, indicating the equivalence of all three phosphorus atoms. The observed $^{31}$P NMR chemical shifts are comparable with those reported values for cis isomers of $\lambda^3$-[EtNP(OR)]$_3$ (R = −C$_6$H$_4$-Br-2).[12]

**Single-Crystal X-Ray Structure of *cis*-$\lambda^3$-[EtNP(OAr)]$_3$ (3a−5a).** The molecular structures of **3a**−**5a** are shown in Figure 2 (top). Selected structural parameters are summarized in Table 1. The molecule exists as a six-membered P$_3$N$_3$ ring in the cis isomeric form. The six-membered ring adopts a flattened-chair conformation with a crystallographic 3-fold axis running through the center of the six-membered ring (Figure 2). Each phosphorus center is attached to two

**Table 1.** Comparison of Structural Data for $\lambda^3$ and $\lambda^5$-Cyclotriphosphazanes

| compounds | ring conf | P−N, Å | P−O, Å | P═E, Å | P−N−P° | N−P−N° | ΣN° |
|---|---|---|---|---|---|---|---|
| | | | $\lambda^3$-Cyclotriphosphazanes | | | | |
| *cis*-$[EtNP(OC_6H_3{}^iPr_2\text{-}2,6)]_3$ (**3a**) | flattened-chair | 1.697(4) | 1.675(4) | | 136.3(2) | 102.1(2) | 359.9 |
| *cis*-$[EtNP(OC_6H_2Me_3\text{-}2,4,6)]_3$ (**4a**) | flattened-chair | 1.688(4) | 1.676(3) | | 136.4(2) | 101.6(2) | 359.0 |
| *cis*-$[EtNP(OC_6H_3Me_2\text{-}2,6)]_3$ (**5a**) | flattened-chair | 1.692(2) | 1.676(2) | | 135.7(1) | 101.6(1) | 359.2 |
| | | | $\lambda^5$-Cyclotriphosphazanes | | | | |
| $[EtNP(S)(OC_6H_3Me_2\text{-}2,6)]_3$ (**11**) | twist-boat | 1.693(3) | 1.603(2) | 1.910(1)[a] | 119.7(2) | 102.3(1) | 355.6 |
| $[EtNP(Se)(OC_6H_3{}^iPr_2\text{-}2,6)]_3$ (**12**) | twist-boat | 1.687(4) | 1.602(3) | 2.064(1)[b] | 121.2(2) | 101.6(2) | 355.1 |
| $[Et_3N_3P_3(OR)_3Se_2]$ (R = $-C_6H_3{}^iPr_2$-2,6) (**14**) | twist-boat | 1.701(3) | 1.620(2) | 2.070(1) | 120.2(2) | 105.9(1) | 353.8 |

[a] E = S. [b] E = Se.

$-NCH_2CH_3$ moietie, and an aryloxide $-OC_6H_3{}^iPr_2$-2,6. The aryloxy substituents on all three phosphorus atoms lie on one side of the ring, while the ethyl groups on the nitrogen atoms are placed on other side. The aryloxide on phosphorus occupies the axial position and is tilted away from the ring. Thus, the lone pair electron on phosphorus is placed on the equatorial position. As a result, the molecule forms a propeller-like structure with 3-fold symmetry.

There are two different P−N bond lengths in the six-membered ring (1.685 and 1.703 Å). The observed average P−N bond lengths lie between the accepted P−N single bond (1.75−1.80 Å)[14] and P═N double bond (1.47−1.55 Å) distances[15] but are comparable with the reported P−N bond lengths for other similar cyclotriphosphazanes, $\lambda^3$-$[EtNP(OR)]_3$.[2c,12] This observation is consistent with the proposed multiple bonding in P−N compounds (vide infra). The observed P−O bond length in **3a** (1.675 Å) is considerably shorter than the P−O single bond length of 1.71 Å,[16] but longer than P═O bonds.[17] The ring nitrogen atoms adopt a near planar geometry (sum of bond angles 359.9°), while the phosphorus atom exists in a distorted tetrahedral geometry.

The solid-state structure of **4a** (Figure 2, middle) is analogous to that of **3a**. The major difference in the structure of **4a** is that it lacks the 3-fold symmetry exhibited by **3a**, and hence the asymmetric part of the unit cell of **4a** contains a full molecule of **4a**. The molecule exists in a propeller-like structure with a cis isomeric form as in the case of **3a** (Figure 2). The average P−N (1.688 Å) and P−O (1.676 Å) bond distances are in agreement with the literature reports,[2c] and those described for **3a** above. The P−N−P and N−P−N bond angles are in the ranges 135.8−137.4° and 101.2−102.2°, respectively. The sum angles around one of the ring nitrogen atoms show a small deviation from planarity, while the other two ring nitrogen atoms are planar. The molecular structure of **5a** is very similar to both **3a** and **4a** (Figure 2, bottom). The P−N bond lengths within the ring are almost equal (1.687−1.696 Å). The average P−O bond distance is 1.676 Å. The average P−N−P (135.7°) and N−P−N (101.6°) bond angles are similar to those of **3a** and **4a**. The sum of bond angles around the nitrogen suggests a trigonal-planar geometry.

**Conformational Preferences for $\lambda^3$-Cyclotriphosphazanes.** The preference for the triaxial chair (chair-*aaa*) has been previously rationalized on the basis of *the gauche effect*.[2c] On this basis, a chair-*aaa* conformer would have favorable orthogonal orientation between the phosphorus and nitrogen lone pairs, while in the boat-*aaa* conformer, the eclipsing interactions would be minimized but not completely eliminated. However, 1,3-dipolar repulsions between the substituents on phosphorus lead to destabilization of the ring in the chair-*aaa* form versus in the boat-*aaa* conformation. Similarly, placing three bulky −OR substituents on the same side of the $P_3N_3$ ring would also lead to an enormous amount of steric repulsions. Hence, it is expected that compounds **3**−**5** bearing very large bulky aryloxy substituents would ideally exist in the boat-*aaa* form where considerable reduction in 1,3-dipolar repulsions and steric repulsions is possible. The fact that, in spite of having very bulky substituents, compounds **3**−**5** crystallize preferentially only as the chair-*aaa* conformer indicates that negative hyperconjugative interactions involving a nitrogen lone pair and an adjacent P−O $\sigma^*$ orbital plays a decisive role in determining the final conformation of the product isolated. For the negative hyperconjugative interactions to be fully efficient, a value close to 90° for the C−N−P−O dihedral angle is ideal. The observed C−N−P−O dihedral angles for **3a**−**5a** indeed are close to 90° (see the Supporting Information, Table S3).

**Oxidation Reactions of *cis*-$\lambda^3$-Cyclotriphosphazanes.** Alkoxycyclophosphazenes (e.g., $N_3P_3(OMe)_6$) when heated alone or in the presence of an alkyl halide undergo a rearrangement to twist-boat N-alkyloxocyclophosphazanes (e.g., $[MeNP(O)(OMe)]_3$).[18] However, there are only two reports on the direct oxidation of $\lambda^3$-cyclotriphosphazanes, $[RNPR']_3$,[19,20] and no studies on the higher chalcogenides of cyclotriphosphazanes such as sulfides, selenides, and

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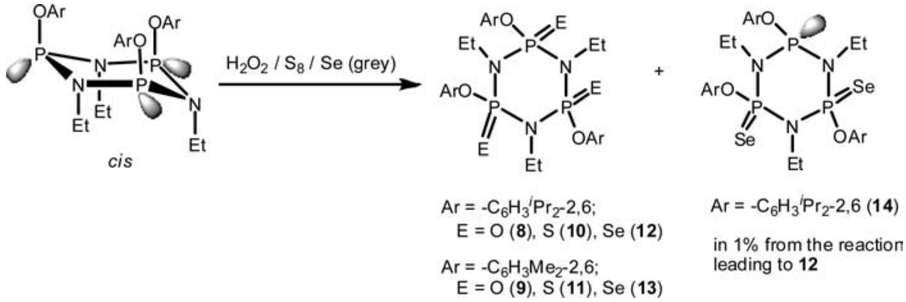
**Scheme 3.** Synthesis of **8**−**14**



tellurides. Hence, in order to study conformational preferences of $\lambda^5$-cyclotriphosphazanes [EtNP(E)R]$_3$, we have carried out oxidation reactions of $\lambda^3$-[EtNP(OR)]$_3$ (R = −$C_6H_3{}^iPr_2$-2,6 (**3a**), −$C_6H_3Me_2$-2,6 (**5a**)) with an excess of 30% *aqueous* $H_2O_2$, elemental sulfur, or selenium and isolated $\lambda^5$-[EtNP(E)OR]$_3$ (R = −$C_6H_3{}^iPr_2$-2,6, *E* = O (**8**), S (**10**), and Se (**12**); R = −$C_6H_3Me_2$-2,6, E = O (**9**), S (**11**), and Se (**13**)) in good yields (Scheme 3).

The cyclotriphosphazane tellurides could not be obtained by the direct oxidation of $\lambda^3$-[EtNP(OR)]$_3$ with elemental tellurium in boiling toluene even after 15 days. In the case of the preparation of **12**, after the removal of the crystals of **12**, the solution was left for crystallization for a further period during which very small quantities of a second product, **14**, were obtained (vide infra). Although the isolated quantity of **14** was not sufficient for an extensive spectral characterization, a single-crystal X-ray diffraction study and the $^{31}$P NMR spectroscopic studies of the original mixture revealed this product to be the diselenide [$Et_3N_3P_3(OR)_3Se_2$] (R = −$C_6H_3{}^iPr_2$-2,6; **14**; Scheme 3). Compounds **8**−**14** have been characterized on the basis of their spectral properties (IR, $^1$H, $^{31}$P, and $^{77}$Se NMR) and single-crystal X-ray diffraction studies. The IR spectra of **8** and **9** show a very strong band at 1275 cm$^{-1}$ for the P=O stretching vibration.[8] The $^1$H NMR spectra of all six compounds exhibit the expected resonances for phenyl protons ($\delta$ 6.9−7.2), −NEt groups (at $\delta$ 1.3−1.6 for (C$H_3$) and $\delta$ 3.5−4.0 for (C$H_2$)), the $^i$Pr protons (in the case of **3a** at $\delta$ 1.3 (C$H_3$) and in the range 3.5−4.6 (C$H$)), and methyl protons (for **5a** at $\delta$ 2.4−2.5 (C$H_3$)).

The $^{31}$P NMR spectra of the trichalcogenide derivatives show singlets at $\delta$ 0.11 (**8**), −2.5 (**9**), 64.4 (**10**), 60.1 (**11**), 64.5 (**12**), and 59.2 (**13**) (see the Supporting Information, Table S1). The chemical shift values of the trioxo derivatives **8** and **9** are nearly $\delta$ 90 upfield-shifted from the parent $\lambda^3$ compounds **3a** and **5a** respectively. On the other hand, the trisulfide and triselenide derivatives **10**−**13** are only about $\delta$ 30 upfield-shifted compared to the parent molecules. Owing to the coupling between phosphorus and selenium nuclei, the triselenide derivatives **12** and **13** show satellite peaks in the $^{31}$P NMR spectrum ($^1J_{PSe}$ = 956 and 959 Hz, for **12** and **13**). Compound **14** shows an $A_2X$ pattern with the "A"-type $\lambda^5$-phosphorus nuclei appearing as a doublet in the upfield at $\delta$ 66.2 (Figure S1, see the Supporting Information). The "X"-type $\lambda^3$-phosphorus appears as a triplet in the downfield at $\delta$ 138.5, with a $J_{AX}$ of 8 Hz. It is interesting to note that the signal due to the unoxidized phosphorus in **14** is ca. $\delta$ 46.3 downfield-shifted from the $^{31}$P NMR signal for parent compound **5a**. The $^{77}$Se NMR spectrum of **12** consists of a doublet centered at $\delta$ −143.5 (d, $^1J_{SeP}$ = 957 Hz). Compound **13** resonates at $\delta$ −142.5 (d, $^1J_{SeP}$ = 960 Hz) as a doublet (see the Supporting Information, Figure S2).

**Single-Crystal X-Ray Structure of $\lambda^5$-[EtNP(S)(OC$_6$H$_3$Me$_2$-2,6)]$_3$ (11).** The structure of **11** (Figure 3) contains a six-membered $P_3N_3$ ring in a twist-boat conformation. The "prow" and "stern" positions are occupied by P(3) and N(1), respectively. Each phosphorus atom is connected to two nitrogen, one sulfur, and one −$OC_6H_3Me_2$-2,6 group. The nitrogen atoms are surrounded by one ethyl group and two phosphorus moieties. The −$OC_6H_3Me_2$-2,6 group on the phosphorus and N(1) ethyl group lie on the same side of the six-membered $P_3N_3$ ring. The sulfur atoms and two of the ethyl groups on the nitrogen atoms (N(2) and N(3)) are on the other side of the ring (Figure 3). The P−N bond lengths (av. 1.693(3) Å; Table 1) are in very good agreement with the corresponding lengths in $\lambda^5$-[EtNP(O)(OR)]$_3$.[20] The average of the P−N bond lengths suggests that these bonds are not pure single bonds.[14] A certain degree of $\pi$ bonding still exists in the $N_3P_3$-phosphazane ring skeleton. The average P=O (1.603(2) Å)[16] and P=S (1.910(1) Å)[21] bond lengths are in the expected range. The geometry at the phosphorus centers is distorted tetrahedral with bond angles varying from 99.9(1) to 119.2(2)°. The nitrogen atoms have a planar environment with bond angles of 115.6(2)−124.7(2)°. The average N−P−N angles (102.3(1)°) and the P−N−P angles (119.7(2)°) are in the expected range.[20]

**Single-Crystal X-Ray Structure of $\lambda^5$-[EtNP(Se)(OC$_6$H$_3{}^i$Pr$_2$-2,6)]$_3$ (12).** A perspective view of molecule **12** is shown in Figure 3. The core of the molecular structure consists of a six-membered ring composed of three phosphorus and nitrogen atoms. The ethyl group on each nitrogen center and the −$OC_6H_3{}^iPr_2$-2,6 group and selenium atom on each phosphorus center complete the twist-boat conformation (Figure 3). Despite the twist, aryloxy substituents −$OC_6H_3{}^iPr_2$-2,6 on the phosphorus atoms lie on one side of the ring, and ethyl groups on the nitrogen atoms are on other side. The

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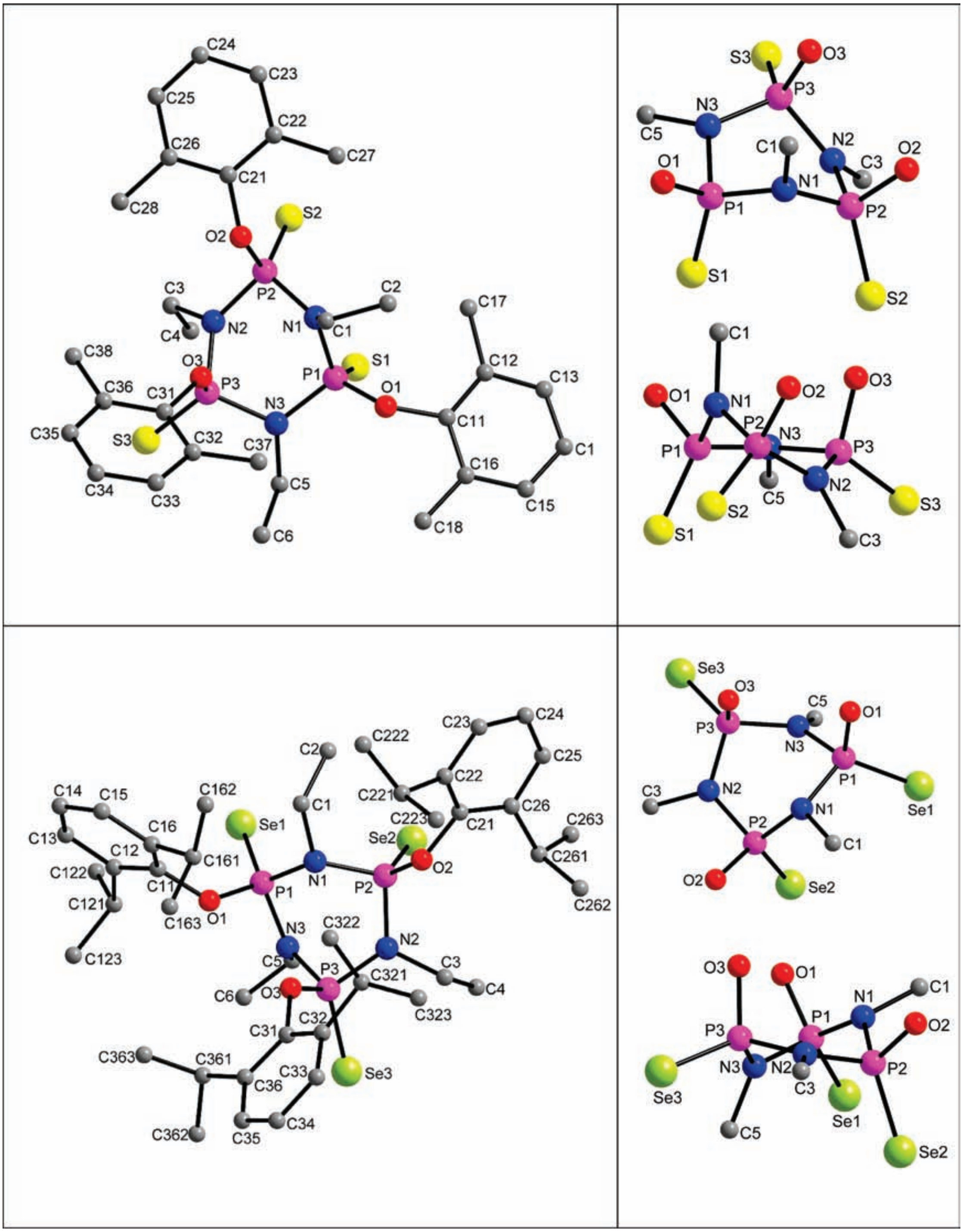


**Figure 3.** Molecular structure and ring conformations of $\lambda^5$-[EtNP(S)(OC$_6$H$_3$Me$_2$-2,6)]$_3$ (**11**) (top) and $\lambda^5$-[EtNP(Se)(OC$_6$H$_3{}^i$Pr$_2$-2,6)]$_3$ (**12**) (bottom).

P−N bond distances are in ca. 1.687(4) Å and compare well to those reported for related compounds.[17,18] The average P−O (1.602(3) Å)[16,20] and P═Se (2.064(1) Å)[21] bond distances are in agreement with the literature precedents. The average N−P−N angles (101.6(2)°) and the P−N−P angles (121.2(2)°) are in the expected range.[20] Distorted tetrahedral geometries were retained around the phosphorus atoms, while the geometry around the nitrogen atoms is nearly planar.

**Single-Crystal X-Ray Structure of $\lambda^5$-[Et$_3$N$_3$P$_3$(OR)$_3$Se$_2$] (R = −C$_6$H$_3{}^i$Pr$_2$-2,6) (14).** The structure of **14** is composed of a phosphorus and nitrogen cyclic six-membered core (Figure 4). The ring is in a twist-boat conformation with crystallographically distinguishable P−N bonds. The orientation of the aryloxy substituents −OC$_6$H$_3{}^i$Pr$_2$-2,6 on the phosphorus atom and ethyl groups on the nitrogen atom of **14** are similar to that of compound **12**. However, compound **14** consists of two pentavalent (P═Se) and one trivalent phosphorus. The selenium substituent occupies the equatorial position with respect to the axial aryloxides. The lone pair of trivalent phosphorus also appears to be occupying the equatorial positions, consistent with the gauche effect described vide supra. The geometrical parameters of the six-membered ring fit well in the range observed for **12** and related compounds.[20]

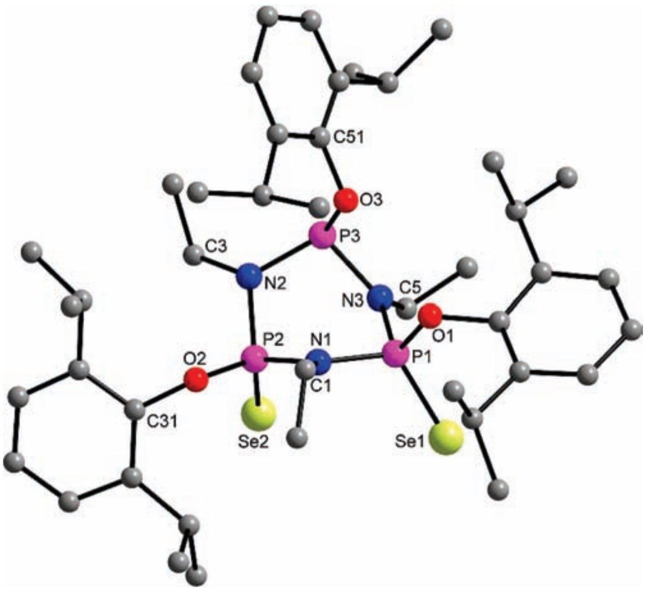
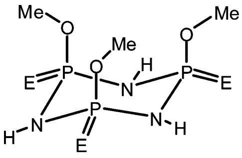


**Figure 4.** Molecular structure of $\lambda^5$-$[Et_3N_3P_3(OR)_3Se_2]$ (R = $-C_6H_3{}^iPr_2$-2,6) (**14**).

**Comparison and Summary of the Crystal Structures.** A comparison of the key structural features of the compounds prepared in the present study is compiled in Table 1. The $P_3N_3$ ring in the molecular structures of **3a**−**5a** exists in a chair (*aaa*) conformation with cis isomeric form. The bond lengths and angles of **3a**, **4a**, and **5a** are comparable with each other and those of other $\lambda^3$-cyclotriphosphazanes $[EtNP(OR)]_3$. The reaction of **3a**/**5a** with elemental sulfur/selenium produces the oxidized products, which contain the $P_3N_3$ ring in the twist-boat conformation. The ring conformations observed in **11**, **12** and **14** are different from those for $\lambda^3$-cyclotriphosphazanes **3a**−**5a**. The bond lengths and angles of $\lambda^5$-cyclotriphosphazanes are again comparable to each other. The P−N bond lengths and N−P−N bond angles of **11** and **12** are comparable with those of **3a**−**5a**. However, the P−O bond lengths of **11** and **12** are slightly shorter to those found for **3a**−**5a**. In the case of compound **12**, the P−N−P angle is considerably smaller than that for compound **5a**. It is important to note that the molecular structures of **11**, **12**, and **14** represent the first examples of trisulfide, triselenide, and diselenide derivatives of $\lambda^5$-cyclotriphosphazanes, respectively. Mean plane calculations indicate that the observed deviations for $\lambda^5$-cyclotriphosphazanes (**11**, **12**, and **14**) are considerably larger than those for $\lambda^3$-cyclotriphosphazanes (**3a**, **4a**, and **5a**; see the Supporting Information, Table S4). In addition, two nitrogen atoms of the $\lambda^5$-cyclotriphosphazane show considerable deviations from the mean plane, which leads to the irregular conformation. Clearly, more studies are necessary on the pentavalent systems before any generalizations could be made regarding the ring shape and conformational preferences.

**Density Functional Theory Studies on $\lambda^5$-$[HNP(S)(OCH_3)]_3$ (15) and $\lambda^5$-$[HNP(Se)(OCH_3)]_3$ (16).** The electronic factors contributing to conformational preferences have been probed by DFT calculations using the B3LYP method in conjunction with the 6-31+G* basis set. The calculations were performed on model systems by replacing the ethyl and aryl groups on nitrogen and phosphorus with hydrogen and methyl groups, respectively. While the steric factors due to the ortho aryl substituents in the experimentally studied systems are not likely to be well represented in these model systems, electronic factors are expected to remain nearly the same.

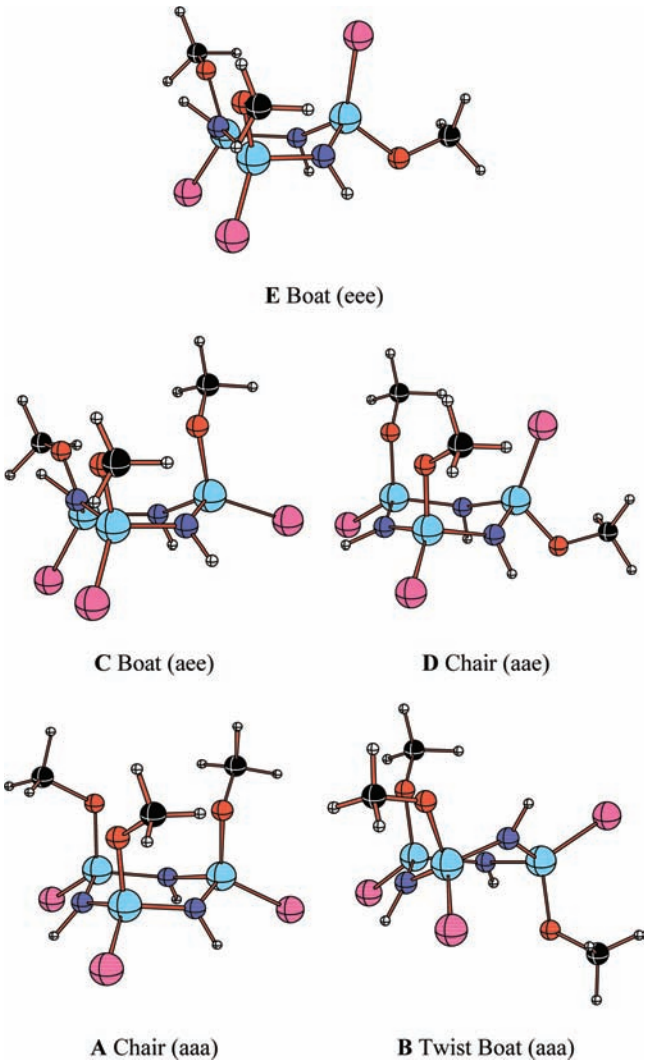
**Scheme 4.** Model Systems Studied Using the B3LYP/6-31G* Level of Theory



E= S **15**; E= Se **16**

Two kinds of $\lambda^5$-cyclotriphosphazane systems are considered for the present investigation, as shown in Scheme 4, differing in their exocyclic substituent (E = S or Se). A large number of possible ring conformations such as chair, boat, twist-boat, and so on can be envisaged for these molecules. Consideration of both cis and trans isomers based on the substituent dispositions, either as axial or equatorial, opens up an even larger isomeric manifold. First, we have carried out an exhaustive conformational search at the HF/6-31G* level of theory. We were able to locate several low-energy conformers and characterize those as minima on the potential energy surface within a range of 7−10 kcal/mol relative to the lowest-energy conformer. All such unique structures were then reoptimized at the B3LYP/6-31+G* level of theory.

The optimized geometries in the case of the sulfur derivative are provided in Figure 5. It is noticed that the P−N ring in general adopts either a chair or a boat conformation that is energetically closely spaced. In the lowest-energy conformer (**15A** and **16A**), the six-membered P−N ring exists in a chair arrangement with axially oriented −OMe substituents on phosphorus. Interestingly, another isomer, **D**, with triaxial −OMe substitution is more than 6 and 8 kcal/mol higher than **A** respectively for E = S and Se. The major difference between these two configurations is the orientation of the P−OMe groups. In **D**, one of the −OMe groups is oriented toward the equatorial position, while all −OMe groups are axial in **A**. Further, a cyclic network of intramolecular hydrogen bonding between the methyl groups and the OMe oxygen is identified in **D**. This situation is disrupted when one of the −OMe groups occupies the equatorial position, as in **D**. Although additional hydrogen bonding between the N−H groups and the oxygen of the equatorial OMe group is evident, the net effect of axial disposition of the P═S group appears destabilizing. The general trend from the computed relative energies (see the Supporting Information, Table S5) indicates that the axial orientation of the OMe group is preferred. For instance, the energies of structures **D** and **E** are higher than those of **A**, **B**, and **C**. It can also be noticed that the preference toward a chair conformation of the P−N ring system largely depends on the orientation of the −OMe group. In the case of triaxial arrangement of −OMe groups, as in **A** and **C**, the energy differences between the lowest-energy chair and nearest boat conformer are of the order of 3.4 (E = S) and 6.4 (E = Se)


E Boat (eee)

C Boat (aee)

D Chair (aae)

A Chair (aaa)

B Twist Boat (aaa)

**Figure 5.** The B3LYP/6-31+G* optimized geometries of the lower-energy structures of $\lambda^5$-[HNP(S)($OCH_3$)]$_3$ (**15**) (light blue, P; dark blue, N; red, O; pink, S; black, C). Similar geometries are also noticed for $\lambda^5$-[HNP(Se)($OCH_3$)]$_3$ (**16**).

kcal/mol. The energetic preference for a particular structure (configuration and conformation) is more pronounced in the case of exocyclic selenium (**16**) than that with sulfur (**15**). Another interesting structural feature relates to the degree of pyramidalization at the nitrogen centers of the cyclophosphazane rings.[22] It is generally found that the larger degree of pyramidalization is noticed in higher-energy structures such as **D** and **E**. This observation alludes to the influence of nitrogen lone pair delocalization toward the relative stabilities of various configurations and conformers of these P−N ring systems.

Inspection of optimized geometric parameters reveals that the average P−N bond distances (in **A** to **E**) are around 1.70 Å (see Tables S6 and S7 in the Supporting Information). These values are in general slightly shorter than the normal P−N single-bond distances, but are comparable to the experimentally observed values in the present study (Table 1). It has been shown previously that negative hyperconjugation could increase the $\pi$-bonding character between atoms from which the lone pair is delocalizing and its adjacent atom with which negative hyperconjugation is operating.[23] There will be a concomitant increase in the $\sigma$ bond length due to higher population of the corresponding antibonding orbital. Another important factor that presumably influences the bond lengths in these molecules is the high charge on phosphorus, which in turn can decrease the effective covalent radius of phosphorus, thereby changing the P−N bond lengths.[24]

To examine the importance of lone pair delocalization toward the conformational preference of cyclophosphazanes, natural bond orbital (NBO) analysis was performed using the wave functions generated at the B3LYP/6-31+G* level. Three kinds of lone pairs are identified on S and Se in the Lewis-type description as given by the NBO. Two of these are *p*-type lone pairs, and the third one is a $\sigma$-type lone pair. Interestingly, the *p*-type lone-pair electrons are found to be relatively more depleted due to delocalization into the vicinal BD* of P−OMe/P═E (one BD* of P−O and a pair of BD*'s of P═E) bonds.[25] The examination of nitrogen lone pair populations reveals a high degree of delocalization with the vicinal antibonding orbitals. The nitrogen lone pair delocalization with the adjacent vicinal antibonding orbitals in general is found to be better with the lower-energy conformers. For instance, the sum of the second-order perturbative stabilization corresponding to the N lone pair delocalization into the vicinal P−O/Se bonds in **A** is found to be higher than that in **B**. A similar observation in favor of the chair-*aaa* conformer is found with the E = Se system as well. The conformational preference as noticed here might change depending on the extent of steric interactions caused by the subsitutents on nitrogen as well as the oxygen of the −OR group. However, a balance between cumulative steric and electronic effects would decide the conformational preference exhibited by these cylic phosphazanes.

## Conclusion

It has been demonstrated that the reaction between a kinetically stabilized organosilanetriol and a highly reactive $\lambda^3$-cyclotriphosphazane offers easy access to a unique molecular silicophosphonate with an abundant number of acidic hydroxyl groups. The reaction between acidic-proton-containing aryloxides and $\lambda^3$-cyclotriphosphazane yields sterically encumbered *cis*-aryloxy $\lambda^3$-cyclotriphosphazanes where the six-membered ring remains intact. The oxidation of $\lambda^3$-cyclotriphosphazanes yields chalcogenide derivatives,

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[22] Full details of the degree of pyramidalization (calculated as the difference between a fully planar situation (angle = 360°) and the sum of angles around the nitrogen atom) along with other structural parameters are summarized in the Supporting Information.

[23] Reed, A. E.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1990**, *112*, 1434.

[24] Analyses of charge distribution using the natural population analyses exhibited fairly high charges on phosphorus, which ranges from +1.89 to +1.92 with the P−S systems, while the variation is found to be somewhat less pronounced with the P−Se systems, having variations from +1.82 to +1.84. In all of these molecules, 3d orbital contribution towards bonding was found to be only about 0.09, as revealed by the natural electronic contribution. This implies that the d orbital is mainly acting as a polarization function, and it is playing only a secondary role in bonding. In both cases, phosphorus was found to have four highly polarized $\sigma$ natural bond orbitals.

[25] See Supporting Informationfor a detailed list of NBO delocalizations.

**Table 2.** Crystal Data and Details of Structure Refinement

| | **3a** | **4a** | **5a** | **11** | **12** | **14** |
|---|---|---|---|---|---|---|
| empirical formula | $C_{42}H_{66}N_3O_3P_3$ | $C_{33}H_{48}N_3O_3P_3$ | $C_{30}H_{42}\ N_3O_3P_3$ | $C_{30}H_{42}N_3O_3P_3S_3$ | $C_{42}H_{66}N_3O_3P_3Se_3$ | $C_{42}H_{66}N_3O_3P_3Se_2$ |
| fw | 753.89 | 627.65 | 585.58 | 681.76 | 990.77 | 911.81 |
| temp, K | 200(2) | 293(2) | 293(2) | 293(2) | 293(2) | 133(2) |
| diffractometer | STOE-AED2 | Nonius-MACH3 | Nonius-MACH3 | STOE-AED2 | Nonius-MACH3 | STOE-AED2 |
| wavelength, Å | 0.71073 | 0.71069 | 0.71069 | 0.71073 | 0.71073 | 0.71073 |
| cryst syst | cubic | triclinic | monoclinic | monoclinic | monoclinic | triclinic |
| space group | $P4_3n$ | $P\bar{1}$ | $P2_1/n$ | $P2_1/n$ | $P2_1/c$ | $P\bar{1}$ |
| $a$, Å | 21.975(2) | 8.3291(2) | 8.5910(2) | 11.547(2) | 18.652(3) | 10.699(2) |
| $b$, Å | | 12.8684(1) | 19.2723(2) | 15.144(3) | 9.850 (2) | 13.772(3) |
| $c$, Å | | 17.5186(1) | 20.150(2) | 19.175(4) | 25.85(5) | 16.160(3) |
| $\alpha$, deg | | 74.354(7) | | | | 82.50(3) |
| $\beta$, deg | | 82.157(1) | 101.520(1) | 101.10(3) | 93.45(2) | 87.05(3) |
| $\gamma$, deg | | 89.252(1) | | | | 70.99(3) |
| $V$, Å$^3$ | 10612.2(2) | 1790.6(4) | 3269.0(7) | 3290.3(11) | 4741(10) | 2231.9(8) |
| $Z$ | 8 | 2 | 4 | 4 | 4 | 2 |
| $D_{calcd}$, Mg/m$^3$ | 0.944 | 1.164 | 1.190 | 1.376 | 1.388 | 1.357 |
| abs coeff, mm$^{-1}$ | 0.144 | 0.201 | 0.215 | 0.408 | 2.467 | 1.804 |
| $F(000)$ | 3264 | 672 | 1248 | 1440 | 2040 | 952 |
| cryst size, mm$^3$ | 0.7 × 0.7 × 0.7 | 0.6 × 0.3 × 0.3 | 0.5 × 0.5 × 0.4 | 0.5 × 0.2 × 0.2 | 0.4 × 0.33 × 0.2 | 0.3 × 0.3 × 0.2 |
| $\theta$ range, deg | 3.71 to 25.02 | 1.22 to 25.00 | 1.48 to 25.00 | 1.73 to 27.34 | 1.09 to 25.01 | 2.01 to 24.75 |
| data/restraints/params | 1694/0/159 | 6306/0/391 | 5752/0/361 | 6925/0/400 | 8348/0/508 | 7568/0/478 |
| goodness-of-fit on $F^2$ | 1.084 | 0.930 | 1.093 | 1.036 | 1.052 | 1.017 |
| $R_1$ [$I > 2\sigma(I)$] | 0.0574 | 0.0690 | 0.0518 | 0.0579 | 0.0394 | 0.0384 |
| $R_2$ [$I > 2\sigma(I)$] | 0.1337 | 0.1650 | 0.1445 | 0.1522 | 0.0878 | 0.0918 |

where the $P_3N_3$ ring changes from the chair to a twist-boat form. Apart from the isolation of the first example of trisulfide and triselenide derivatives, it is also possible to obtain partially selenized derivative **14** and obtain its crystal structure. The experimentally observed conformational features of these molecules have been rationalized with the help of DFT-optimized geometries of model systems. The agreement between the computed and the experimentally geometric parameters has been good. It has been identified that the lower-energy conformers tend to adopt a chair or boat P−N ring system with a triaxial disposition of the −OR group.

## Experimental Section

**Apparatus.** All reactions were carried out under an inert atmosphere of purified nitrogen using standard Schlenk line techniques. The $^1H$ ($Me_4Si$ internal standard) and $^{31}P$ (85% $H_3PO_4$ external standard) NMR spectra were recorded on a Varian VXR 300S spectrometer. Infrared spectra were obtained on a Perkin-Elmer FT-IR spectrometer. Microanalyses were performed on a Thermo Finnigan (FLASH EA 1112) microanalyzer. The EI mass spectra were obtained on Finnigan MAT System 8230, Varian MAT CH5, and Perkin-Elmer Clarus 500 GC-MS mass spectrometers.

**Chemicals.** Dichloromethane, petroleum ether (60−80 °C), benzene, toluene, acetonitrile, and tetrahydrofuran were purified and dried by standard procedures.[26] The pyrophoric and moisture-sensitive $\lambda^3$-cyclotriphosphazane $[EtNPCl]_3$ (**1**) was synthesized as described in the literature.[2c,27] 2,6-$^i$Pr$_2$C$_6$H$_3$N(SiMe$_3$)Si(OH)$_3$ was synthesized as described previously.[7a] Ethylamine hydrochloride (Aldrich), phosphorus trichloride (Spectrochem), trimethyl aluminum (1.6 M solution in hexane, Aldrich), sodium metal (Rankem), hydrogen peroxide (30% w/v, Loba Chemie), sulfur (S. D. Fine), selenium (Schuchardt), tellurium (Schuchardt), 2,6-di-isopropylphenol (Aldrich), 2,4,6-trimethylphenol (Lancaster), 2,6-dimethylphenol (Merck), 4-*tert*-butylphenol (Lancaster), pentafluorophenol (Lancaster), 1-naphthol (S. D. Fine), 2,6-di-*tert*-butyl-4-methylphenol (Spectrochem), and DABCO (Lancaster) were procured from commercial sources and used as received.

**Synthesis of 2.** $\lambda^3$-$[EtNPCl]_3$ (0.66 g, 2 mmol) was added dropwise to a solution of (2,6-$^i$Pr$_2$C$_6$H$_3$)NSiMe$_3$Si(OH)$_3$ (0.66 g, 2 mmol) and $Et_3N$ (0.8 mL, 6 mmol) in petroleum ether (100 mL) at 0 °C. The reaction mixture was slowly brought to room temperature and stirred for 24 h and filtered. The resultant clear solution was concentrated by removing the solvent under reduced pressure. Crystallization of the waxy white solid from dichloromethane/petroleum ether (5:1, v/v) at −18 °C yielded **2** as single crystals. Yield: 0.60 g (35% based on $\lambda^3$-$[EtNPCl]_3$). Mp: 139−141 °C. Anal. calcd for $C_{34}H_{72}N_4O_9P_2Si_4$ (mol wt: 855.26): C, 47.8; H, 8.5; N, 6.6. Found: C, 47.9; H, 8.2; N, 6.8. EI-MS (70 eV): *m/z* 855 (4%, M$^+$). IR (KBr, cm$^{-1}$): $\bar{\upsilon}$ 3612(w), 2973(s), 2407(m), 1657(w), 1552(w), 1453(w), 1256(s), 1190(vs), 1091(vs), 979(vs), 927(vs), 841(vs), 802(s), 762(w), 545(s). $^1H$ NMR (300 MHz, $CDCl_3$): $\delta$ 0.15 (s, 18H, Si$CH_3$), 1.1 (t, 6H, $CH_3CH_2NH_2$), 1.18 (d, 24H, $(CH_3)_2CH$), 1.7 (4H, $NH_2$), 2.7 (q, 4H, $CH_3CH_2NH_2$), 3.5−3.7 (m, 4H, $(CH_3)_2CH$), 5.7 (d, 2H, PH, $^1J_{PH} = 670$ Hz), 7.1 (2H, aryl CH), 7.3 (4H, aryl CH), 8.2 (OH). $^{29}Si$ NMR (99 MHz, $C_6D_6$): $\delta$ 8.1 (s, $SiMe_3$), −82.9 (d, $NSiO_3$, $^2J_{PSi} = 5.5$ Hz). $^{31}P$ NMR (203 MHz, $C_6D_6$): $\delta$ −9.4 (d, $^1J_{PH} = 670$ Hz).

**Synthesis of 3a.** A mixture of sodium (0.42 g, 18 mmol) and 2,6-di-isopropylphenol (1.07 g, 6 mmol) was heated under reflux in THF (70 mL) for 15 h. The resulting solution was filtered to remove the unreacted sodium metal. $\lambda^3$-$[EtNPCl]_3$ (0.66 g, 2 mmol) was added dropwise to the above stirred solution at 0 °C. The reaction mixture was slowly brought to room temperature and heated under reflux for 12 h. After allowing it to stand for 2 h, the precipitated sodium chloride was filtered off. Removal of the solvent under reduced pressure gave an oily product, which was dissolved in petroleum ether (50 mL) and filtered. Removal of the solvent in a vacuum gave pale yellow viscous oil with a cis/trans isomeric mixture of **3** (ratio 1:1). Isomer *cis*-[EtNP(OC$_6$H$_3$$^i$Pr$_2$-2,6)]$_3$ (**3a**) was crystallized from the product mixture in petroleum ether (5 mL) at 0 °C. Yield: 1.22 g (81% based on $\lambda^3$-$[EtNPCl]_3$). Mp: 192−194 °C. Anal. calcd for $C_{42}H_{66}N_3P_3O_3$ (mol wt: 753.91): C,

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66.91; H, 8.82; N, 5.57. Found: C, 66.41; H, 8.76; N, 5.99. EI-MS (70 eV): *m/z* 752 ($M^+$, 2%), 576 ($M^+ - OR$, 32%), 325 ($M^+ - P(OR)_2NEt$, 100%). IR (KBr, $cm^{-1}$): $\bar{\upsilon}$ 3065(m), 2973(vs), 2874(s), 1453(vs), 1380(w), 1328(s), 1202(w), 1176(vs), 1100 (s), 1051(s), 946(vs), 875(w), 841(vs), 775(vs), 716(vs), 650(m), 600(m), 545(w). $^1H$ NMR ($CDCl_3$, 300 MHz): $\delta$ 1.11 (t, 9H, C*H*$_3$, $^3J_{HH} = 7$ Hz), 1.18 (d, 36H, $^i$Pr C*H*$_3$, $^3J_{HH} = 7$ Hz), 3.39−3.51 (m, 6H, C*H*$_2$), 3.81−3.87 (m, 6H, C*H* of $^i$Pr), 7.04−7.14 (m, 9H, aryl C*H*). $^{31}P$ NMR ($CDCl_3$, 121 MHz): $\delta$ 98.9 (s).

**Synthesis of 4a.** The cis−trans isomeric mixture of **4** was synthesized as described above for **3**. A pale yellow viscous oil resulted, with a cis/trans isomer ratio of 4:1. Colorless crystals of isomer *cis*-$[EtNP(OC_6H_2Me_3\text{-}2,4,6)]_3$ (**4a**) were obtained from the isomeric mixture in a petroleum ether/dichloromethane mixture (1/1, v/v). Yield: 0.81 g (65% based on $\lambda^3$-$[EtNPCl]_3$). Mp: 141−143 °C. Anal. calcd for $C_{33}H_{48}N_3P_3O_3$ (mol wt: 627.68): C, 63.15; H, 7.70; N, 6.69. Found: C, 62.97; H, 7.89; N, 6.56. EI-MS (70 eV): *m/z* 626 ($M^+$, 4%), 492 ($M^+ - OR$, 28%), 283 ($M^+ - P(OR)_2NEt$, 100%). IR (KBr, $cm^{-1}$): $\bar{\upsilon}$ 3046(w), 2973(m), 2927(m), 2868(w), 1485(s), 1387(w), 1314(w), 1209(s), 1156(s), 1120(s), 1070(m), 1051(s), 946(vs), 845(m), 814(s), 775(m), 715(m), 683(m), 590(m), 571(m). $^1H$ NMR ($CDCl_3$, 300 MHz): $\delta$ 1.13 (t, 9H, C*H*$_3$, $^3J_{HH} = 7$ Hz), 2.10 (s, 9H, 4-C*H*$_3$ aryl), 2.35 (s, 18H, 2,6-C*H*$_3$ aryl), 3.48−3.62 (m, 6H, C*H*$_2$), 6.77 (s, 6H, aryl C*H*). $^{31}P$ NMR ($CDCl_3$, 121 MHz): $\delta$ 92.1 (s).

**Synthesis of 5a.** The cis−trans isomeric mixture of **5** was synthesized as described above for **3**. A pale yellow viscous oil resulted,with a cis/trans isomer ratio of 1:3.5. The isomer *cis*-$[EtNP(OC_6H_3Me_2\text{-}2,6)]_3$ (**5a**) was crystallized from the product mixture in a petroleum ether/dichloromethane mixture (1/1, v/v). Yield: 0.68 g (58% based on $\lambda^3$-$[EtNPCl]_3$). Mp: 165−167 °C. Anal. calcd for $C_{30}H_{42}N_3P_3O_3$ (mol wt: 589.59): C, 61.53; H, 7.23; N, 7.18. Found: C, 61.80; H, 7.81; N, 6.82. EI-MS (70 eV): *m/z* 584 ($M^+$, 2%), 464 ($M^+ - OR$, 36%), 269 ($M^+ - P(OR)_2NEt$, 100%). IR (KBr, $cm^{-1}$): $\bar{\upsilon}$ 3045(w), 2967(s), 2921(s), 2861(m), 1598(w), 1473(vs), 1387(m), 1321(m), 1275(m), 1175(s), 1163(vs), 1091(s), 1051(s), 946(vs), 854(vs), 768(s), 723(s), 657(w), 590(w), 555(w), 490(w). $^1H$ NMR ($CDCl_3$, 300 MHz): $\delta$ 1.15 (t, 9H, C*H*$_3$, $^3J_{HH} = 7$ Hz), 2.39 (s, 18H, C*H*$_3$ aryl), 3.49−3.58 (m, 6H, C*H*$_2$), 6.88−6.98 (m, 9H, aryl C*H*). $^{31}P$ NMR ($CDCl_3$, 121 MHz): $\delta$ 92.2 (s).

**Synthesis of 6a.** To a stirred solution of sodium salt of 1-naphthol (6 mmol; prepared from 1-naphthol (0.86 g, 6 mmol) and sodium (0.42 g, 18 mmol) in THF (50 mL)) was added $\lambda^3$-$[EtNPCl]_3$ dropwise at 0 °C. The reaction mixture was slowly brought to room temperature and heated under reflux for 15 h. After allowing it to stand for 2 h, the precipitated sodium chloride was filtered off, and the solvent was removed in vacuo. The residue was redissolved in petroleum ether (50 mL) and filtered. Removal of the solvent under reduced pressure gave a dark-brown viscous oil with a cis/trans isomer ratio of 2:1. The isomer **6a** slowly crystallized from the above oil after dissolving it in acetonitrile and leaving it at room temperature. Yield: 0.38 g (29% based on $\lambda^3$-$[EtNPCl]_3$). Mp: 118−120 °C. Anal. calcd for $C_{36}H_{36}N_3P_3O_3$ (mol wt: 651.61): C, 66.36; H, 5.57; N, 6.45. Found: C, 65.74; H, 5.51; N, 7.42. EI-MS (70 eV): *m/z* 653 ($M^+$, 2%), 508 ($M^+ - OR$, 25%), 364 ($M^+ - (OR)_2$, 100%). IR (KBr, $cm^{-1}$): $\bar{\upsilon}$ 3048(w), 2966(m), 2936(m), 2870(w), 1586(s), 1505(s), 1469(s), 1398(vs), 1290(w), 1270(s), 1250(s), 1150(s), 1090(vs), 1052(vs), 1000(m), 945(vs), 890(vs), 800(s), 782(vs), 760(vs), 710(s), 700(s), 695(s), 650(w), 573(m), 520(w). $^1H$ NMR ($CDCl_3$, 300 MHz): $\delta$ 1.27 (t, 9H, C*H*$_3$, $^3J_{HH} = 7$ Hz), 3.60−3.75 (m, 6H, C*H*$_2$), 6.57−8.39 (m, 21H, aryl C*H*). $^{31}P$ NMR ($CDCl_3$, 121 MHz): $\delta$ 94.2 (s).

**Synthesis of 7a.** Compound **7** containing the cis−trans isomeric mixture was synthesized as described above for **3**. A pale yellow viscous oil resulted, with a cis/trans isomer ratio of 1:2.5. Isomer **7a** was crystallized from the mixture in petroleum ether/dichloromethane (1/1, v/v). Yield: 0.46 g (34% based on $\lambda^3$-$[EtNPCl]_3$). Mp: 151−153 °C. Anal. calcd for $C_{36}H_{54}N_3P_3O_3$ (mol wt: 669.76): C, 64.56; H, 8.13; N, 6.27. Found: C, 64.02; H, 8.20; N, 6.05. IR (KBr, $cm^{-1}$): $\bar{\upsilon}$ 2966(s), 2868(m), 1611(w), 1512(s), 1380(w), 1236(vs), 1170(s), 1117(w), 1064(m), 946(vs), 873(vs), 750(m), 742(m), 564(w). $^1H$ NMR ($CDCl_3$, 300 MHz): $\delta$ 1.15 (t, 9H, C*H*$_3$, $^3J_{HH} = 7$ Hz), 1.36 (s, 27H, C*H*$_3$-$^t$Bu), 3.45 (m, 6H, C*H*$_2$), 6.90−7.15 (m, 12H, aryl C*H*). $^{31}P$ NMR ($CDCl_3$, 121 MHz): $\delta$ 98.2 (s).

**Synthesis of cis 8 and 9.** To a vigorously stirred solution of **3a** (0.1 g, 0.13 mmol) or **5a** (0.1 g, 0.17 mmol) in MeOH (30 mL)/THF (50 mL) was added 30% aq $H_2O_2$ (1 mL) dropwise at 0 °C. The reaction mixture was slowly brought to room temperature and stirred for 24 h. The solvent was removed, and the resultant crude product was dissolved in dichloromethane (50 mL) and dried over sodium sulfate. An analytically pure compound was crystallized from acetonitrile solution at room temperature. *Compound* **8**. Yield: 0.03 g (31% based on **3a**). Mp: 175−177 °C. Anal. calcd for $C_{42}H_{66}N_3P_3O_6$ (mol wt: 801.91): C, 62.91; H, 8.30; N, 5.24. Found: C, 63.42; H, 8.49; N, 5.54. IR (KBr, $cm^{-1}$): $\bar{\upsilon}$ 2973(s), 2930(m), 2874(w), 1479(w), 1341(m), 1275(vs), 1200(w), 1150(m), 1110(vs), 1018(vs), 920(m), 900(s), 814(vs), 709(m), 577(w), 490(w), 450(w). $^1H$ NMR ($CDCl_3$, 300 MHz): $\delta$ 1.25−1.27 (d, 36H, $^i$Pr C*H*$_3$, $^3J_{HH} = 7$ Hz), 1.32−1.39 (t, 9H, C*H*$_3$, $^3J_{HH} = 7$ Hz), 3.54−3.61 (m, 12H, C*H*$_2$ and C*H*), 7.05, 7.14 (9H, aryl C*H*). $^{31}P$ NMR ($CDCl_3$, 121 MHz): $\delta$ −0.11 (s). *Compound* **9**. Yield: 0.05 g (46% based on **5a**). Mp: 196−198 °C. Anal. calcd for $C_{30}H_{42}N_3P_3O_6$ (mol wt: 633.59): C, 56.51; H, 6.64; N, 6.59. Found: C, 56.77; H, 6.38; N, 5.18. IR (KBr, $cm^{-1}$): $\bar{\upsilon}$ 2966(m), 2927(m), 2854(w), 1485(m), 1341(w), 1275(vs), 1163(s), 1097(s), 1031(vs), 945(m), 919(s), 788(s), 720(w), 571(m) 490(w). $^1H$ NMR ($CDCl_3$, 300 MHz): $\delta$ 1.40−1.47 (t, 9H, C*H*$_3$, $^3J_{HH} = 7$ Hz), 2.44 (s, 18H, C*H*$_3$ aryl), 3.60−3.85 (m, 6H, C*H*$_2$), 6.98, 7.00 (9H, aryl C*H*). $^{31}P$ NMR ($CDCl_3$, 121 MHz): $\delta$ −2.5 (s).

**Synthesis of 10 and 11.** A mixture of **3a** (0.2 g, 0.27 mmol)/**5a** (0.14 g, 0.24 mmol) and sulfur powder (0.40 g, 12.5 mmol) was heated under reflux in toluene (40 mL) for 7 days. Subsequently, the reaction mixture was brought to room temperature and concentrated to 5 mL. The colorless crystals of **10** and **11** were obtained with unreacted sulfur at 0 °C. The unreacted sulfur was removed from the product by hand-picking under a microscope. *Compound* **10**. Yield: 0.11 g (48% based on **3a**). Mp: 214−216 °C. Anal. calcd for $C_{42}H_{66}N_3P_3O_3S_3$ (mol wt: 850.11): C, 59.34; H, 7.83; N, 4.94; S, 11.32. Found: C, 58.52; H, 8.14; N, 5.68; S, 12.29. IR (KBr, $cm^{-1}$): $\bar{\upsilon}$ 3064(w), 2971(s), 2930(m), 2870(m), 1463(m), 1439(m), 1382(w), 1364(w), 1324(w), 1252(w), 1160(s), 1106(m), 1075(s), 1063(m), 1038(s), 928(vs), 898(vs), 772(vs), 717(w), 699(w), 659(w), 611(w). $^1H$ NMR ($CDCl_3$, 400 MHz): $\delta$ 1.24−1.26 (d, 36H, $^i$Pr−C*H*$_3$), 1.50−1.53(t, 9H, C*H*$_3$) 3.48−3.55 (m, 6H, C*H*$_2$), 3.88−3.97 (m, 3H, C*H*), 7.17−7.22 (m, 9H, aryl C*H*). $^{31}P$ NMR ($CDCl_3$, 121 MHz): $\delta$ 64.4 (s). *Compound* **11**. Yield: 0.08 g (51% based on **5a**). Mp: 226−228 °C. Anal. calcd for $C_{30}H_{42}N_3P_3O_3S_3$ (mol wt: 681.79): C, 52.85; H, 6.21; N, 6.16; S, 14.11. Found: C, 53.42; H, 6.42; N, 4.64; S 12.71. IR (KBr, $cm^{-1}$): $\bar{\upsilon}$ 2982(w), 2930(w), 1472(m), 1380(w), 1266(w), 1154(s), 1093(m), 1061(w), 1025(s), 945(vs), 907(vs), 774(s), 704(w), 649(w), 596(w), 477(w), 414(w). $^1H$ NMR ($CDCl_3$, 400 MHz): $\delta$ 1.42−1.44 (t, 9H, C*H*$_3$, $^3J_{HH}$ = 7 Hz), 2.44 (s, 18H, C*H*$_3$ aryl), 3.88−4.0 (m, 6H, C*H*$_2$), 7.03 (s, 9H, aryl C*H*). $^{31}$P NMR (CDCl$_3$, 121 MHz): $\delta$ 60.1 (s).

**Synthesis of 12−14.** A sample of **3a** (0.3 g, 0.40 mmol)/**5a** (0.3 g, 0.51 mmol) and selenium powder (0.47 g, 5.95 mmol) was heated under reflux conditions in a toluene (30 mL) and THF (20 mL) mixture for 7 days. Subsequently, the reaction mixture was brought to room temperature and filtered to remove the unreacted selenium. The filtrate was concentrated to 3 mL to obtain colorless crystals of **12** and **13** at 0 °C. After the removal of the crystals of **12**, the solution was left for crystallization for a further period, during which very small quantities of a second product, **14**, were obtained (vide infra).

**Analytical and Spectroscopic Data for 12.** Colorless crystals. Yield: 0.28 g (71% based on **3a**). Mp: 193−195 °C. Anal. calcd for $C_{42}H_{66}N_3P_3O_3Se_3$ (mol wt: 990.79): C, 50.91; H, 6.71; N, 4.24. Found: C, 52.19; H, 7.56; N, 3.90. IR (KBr, cm$^{-1}$): $\bar{\nu}$ 3063(w), 2969(s), 2929(m), 2869(m), 1462(m), 1437(m), 1382(m), 1362(w), 1323(m), 1255(w), 1157(s), 1097(m), 1037(s), 919(vs), 890(vs), 793(w), 766(vs), 696(w), 535(w). $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 1.24−1.26 (d, 36H, $^i$Pr C*H*$_3$, $^3J_{HH}$ = 7 Hz), 1.57−1.60 (t, 9H, C*H*$_3$, $^3J_{HH}$ = 7 Hz), 3.47−3.60 (m, 3H, C*H*$_2$), 3.90−4.06 (m, 6H, C*H*), 7.18−7.23 (m, 9H, aryl C*H*). $^{31}$P NMR (CDCl$_3$, 121 MHz): $\delta$ 64.5 (s, $^1J_{PSe}$ = 956 Hz).

**Separation of 14 and Spectroscopic Data.** Although the isolated quantity of **14** ( afew single crystals) was insufficient for a thorough characterization, single-crystal X-ray diffraction and $^{31}$P NMR spectroscopic studies revealed this product to be the diselenide [$Et_3N_3P_3(OR)_3Se_2$] (R = $-C_6H_3{}^iPr_2$-2,6) (**14**). $^{31}$P NMR (CDCl$_3$, 121 MHz): $\delta$ 66.2 (d, $^2J_{pp}$ = 8 Hz), 138.5 (t, $^2J_{pp}$ = 8 Hz).

**Analytical and Spectroscopic Data for 13.** Colorless crystals. Yield: 0.30 g (72% based on **5a**). Mp: 204−206 °C. Anal. calcd for $C_{30}H_{42}N_3P_3O_3Se_3$ (mol wt: 822.47): C, 43.83; H, 5.15; N, 5.11. Found: C, 42.37; H, 4.77; N, 4.03. IR (KBr, cm$^{-1}$): $\bar{\nu}$ 3008(w), 2981(w), 2929(w), 1470(m), 1380(w), 1317(m), 1265(w), 1149(vs), 1094(s), 1057(m), 1020(m), 940(vs), 920(vs), 895(vs), 773(vs), 725(m), 681(m), 659(m), 636(w), 558(w), 514(w), 470(w). $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 1.44−1.47 (t, 9H, C*H*$_3$, $^3J_{HH}$ = 7 Hz), 2.45 (s, 18H, C*H*$_3$ aryl), 3.95−4.05 (m, 6H, C*H*$_2$), 7.03 (s, 9H, aryl C*H*). $^{31}$P NMR (CDCl$_3$, 121 MHz): $\delta$ 59.2 (s, $^1J_{PSe}$ = 959 Hz). $^{77}$Se NMR (CDCl$_3$, 57 MHz): $\delta$ −143.5 (d, $^1J_{SeP}$ = 957 Hz).

**Reactions of $\lambda^3$-[EtNP(OR)]$_3$ with Tellurium.** A sample of **3a** (0.27 g, 0.36 mmol)/**5a** (0.3 g, 0.51 mmol) and elemental tellurium (0.69 g, 5.4 mmol) was heated under reflux in toluene (40 mL) and THF (15 mL) for 7 days. Subsequently, the unreacted tellurium was removed by filtration and concentrated to 3 mL. Crystallization at 0 °C affords the unreacted **3a** and **5a**.

**Single-Crystal X-Ray Diffraction Studies.** The structures of **2**, **3a**, **4a**, **5a**, **11**, **12**, and **14** have been established by single-crystal X-ray diffraction studies. Crystals suitable for X-ray diffraction studies were grown from a petroleum ether/dichloromethane mixture for **2**, **3a**, **4a**, and **5a**, and a toluene/THF mixture was used for **11**, **12**, and **14** at 0 °C. Intensity data were collected on a STOE AED-2 four-circle diffractometer for **3a**, **11**, and **14** and on a Nonius MACH-3 four-circle diffractometer for **2**, **4a**, **5a**, and **12**. All calculations were carried out using the programs in the WinGX model.[28] The structure solution was achieved by direct methods, as implemented in SIR-92.[29] The final refinement of the structure was carried out using full least-squares methods on $F^2$ using SHELXL-97.[30] In the structure of **3a**, a void of 1290 A$^3$ (~12% of the unit cell volume) has been found due to the formation of large hydrophobic cavities. In the cases of **4a** and **5a**, the ethyl group attached to one of the phosphorus atoms was found to be severely disordered, giving rise to unreasonable bond distances involving this ethyl group. The crystallographic data collection, structure solution, and refinement for **3a**, **4a**, **5a**, **11**, **12**, and **13** are given in Table 2. The data for **2** have been described in a preliminary communication.[6]

**Computational Methods.** All calculations were performed using the Gaussian 98 suite of quantum chemical programs.[31] The geometry optimizations on a larger group of conformers were first carried out at the HF/6-31G* level of theory. After an elaborate conformation sampling at the Hartree−Fock level of theory, the lower-energy conformers were subsequently taken for higher-level calculations. The gas-phase geometry optimizations employing the density functional theory method using the B3LYP functional[32] in combination with the 6-31+G* basis set were used in the present study. The stationary points thus obtained on the respective potential energy surfaces were characterized at the same level of theory by evaluating the corresponding Hessian indices. All of the conformers were identified as true minima and found to possess only positive frequencies. The relative energies reported in this study are the "bottom-of-the-well" values without the inclusion of thermal or zero-point energy corrections. The wave functions were analyzed further using Weinhold's natural bond orbital method (NBO 3.1) to capture the key electron delocalizations.[33] In the NBO terminology, the bonding and antibonding orbitals generated using the natural orbitals are represented as BD and BD* in the text.

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**Supporting Information Available:** Details of X-ray structure investigations (CIF) and selected structural parameters, mean plane calculations, and details of DFT calculations (PDF).This material is available free of charge via the Internet at http://pubs.acs.org.

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