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Synthesis and Derivatization of the Bis(amido)-λ^3-cyclodiphosphazanes *cis*-[R′(H)NP(μ-NR)]$_2$, Including a Rare Example, *trans*-[*t*Bu(H)N(Se)P(μ-NCy)]$_2$, Showing Intermolecular Se···H–O Hydrogen Bonding

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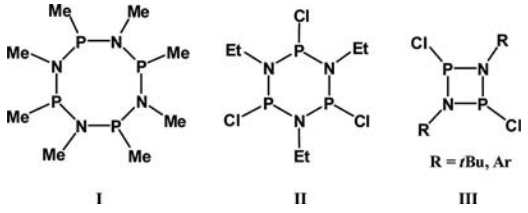
The reaction of PCl_3 with $CyNH_2$ in a 1:3 ratio afforded the dichloro-λ^3-cyclodiphosphazane, *cis*-[ClP(μ-NCy)]$_2$ (**2**), whereas the corresponding 1:5 reaction gave the bis(amido)-λ^3-cyclodiphosphazane *cis*-[Cy(H)NP(μ-NCy)]$_2$ (**3**) in quantitative yield. The dichloro derivative **2** was converted into **3** by reacting **2** with four equivalents of $CyNH_2$. The mixed (amido)derivatives *cis*-[*t*Bu(H)NP(μ-NCy)]$_2$ (**4**) and *cis*-[Cy(H)NP(μ-N*t*Bu)]$_2$ (**5**) were prepared from the reaction of *cis*-[ClP(μ-NCy)]$_2$ (**2**) and *cis*-[ClP(μ-N*t*Bu)]$_2$ (**1a**) with a fourfold excess of the respective primary amines. The oxidation of the bis(amido)-λ^3-cyclodiphosphazanes **3**–**5** with two equivalents of H_2O_2/H_2O, S_8, and Se_8 produced the bis(oxo) [R′(H)N(O)P(μ-NR)]$_2$ [R = R′ = Cy (**6**); R = *t*Bu, R′ = Cy (**7**); R = Cy, R′ = *t*Bu (**8**)], bis(sulfide) [R′(H)N(S)P(μ-NR)]$_2$ [R = R′ = Cy (**9**); R = *t*Bu, R′ = Cy (**10**); R = Cy, R′ = *t*Bu (**11**)], and bis(selenide) [R′(H)N(Se)P(μ-NR)]$_2$ [R = R′ = Cy (**12**); R = *t*Bu, R′ = Cy (**13**); R = Cy, R′ = *t*Bu (**14**)] derivatives, respectively. The reaction of *cis*-[R(H)NP(μ-N*t*Bu)]$_2$ with two equivalents of phosphoryl azide, [$N_3P(O)(OPh)_2$], afforded the corresponding bis(iminophosphoryl) derivatives, *cis*-{R(H)N[(OPh)$_2$-P(O)N]P(μ-N*t*Bu)}$_2$ [R = *t*Bu (**15**), R = Ph (**16**), R = Cy (**17**)]. The solid-state structures for **11**, **12**, **13**, and **15** were determined by single-crystal X-ray diffraction studies. Interestingly, the bis(selenide) derivative [*t*Bu(H)N(Se)P(μ-NCy)]$_2$ **13** turned out be a *trans* isomer in the solid state, whereas the other cyclodiphosphazane derivatives exhibited the *cis* geometry. Compounds **13** and **15** crystallized along with a water molecule that facilitated the intermolecular Se···H–O and N···H–O hydrogen bonding, respectively, to form a linear 1D hydrogen bonding network.

Introduction

Cyclodiphosphazane is a saturated four-membered P_2N_2 ring and is one of the major classes of the cyclic phosphazane compounds. Dichlorocyclodiphosphazanes, *cis*-[ClP(μ-NR)]$_2$, are important starting compounds for the synthesis of a variety of cyclodiphosphazane derivatives by means of nucleophilic substitution reactions at the phosphorus atoms.[1] Dichlorocyclodiphosphazanes are prepared by the reaction of PCl_3 with primary amines (RNH_2) or with amine hydrochlorides (RNH_3Cl). Although the formation of different types of cyclophosphazanes depends to some extent on the stoichiometry and reaction conditions, it mainly depends on the choice of the primary amine employed in the reaction. The cyclic tetramers **I** (Scheme 1)[2] and trimers **II**[3] are formed with methyl- and ethylamines, whereas the formation of cyclic dimers **III**, *cis*-[ClP(μ-NR)]$_2$, and, to some extent, monomeric compounds, such as aminobis(phosphanes), have been observed exclusively with more sterically demanding primary amines such as *t*BuNH$_2$ and ArNH$_2$.[4]



Scheme 1. The different forms of the cyclophosphazanes.

The main group and transition metal chemistry of dianionic bis(amido)cyclodiphosphazane, *cis*-[R′NHP(μ-NR)]$_2$, and its P^V derivatives, *cis*-[R′NHP(E)(μ-NR)]$_2$ (E = O, S, Se, NR), has been extensively studied.[5–7] Even though the bis(amido)-λ^3-cyclodiphosphazanes and the corresponding P^V systems have shown versatile coordination behavior, only *cis*-[*t*BuNHP(μ-N*t*Bu)]$_2$ and its P^V derivative have been investigated thoroughly. The mixed aliphatic/aromatic systems have been studied less.[7a] Another example of a homo-substituted bis(amino)-λ^3-cyclodiphosphazane, *cis*-[Ph(H)NP(μ-NPh)]$_2$, was synthesized by the transamination reaction of P(NEt$_2$)$_3$ with aniline.[8] The 1,3-diphenyl-*cis*-2,4-dianilino-λ^3-cyclodiphosphazane was sparingly soluble in most of the organic solvents, and hence was not as synthetically useful as the aliphatic or mixed aliphatic/aromatic derivatives. This synthetic difficulty can be circumvented by choosing the appropriate primary amines to make cyclodi-

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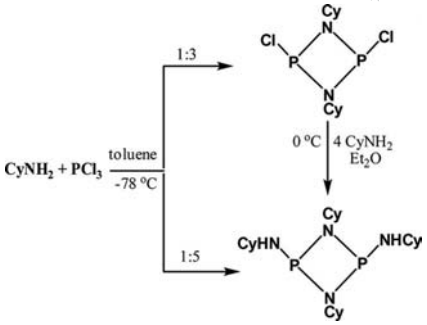
phosphazanes that are soluble in the common organic solvents. As part of our interest in the reactivity and the transition metal chemistry of the cyclodiphosphazanes,[9] and of others,[10] we report herein the synthesis and the crystal structures of new stable and soluble homo- and hetero-substituted bis(amido)-λ³-cyclodiphosphazanes and their chalcogen and imine derivatives. Interestingly, intermolecular Se···H–O hydrogen bonding was observed in the λ⁵-cyclodiphosphazane [*t*Bu(H)N(Se)P(μ-NCy)]$_2$ in the solid state. Although several reports on the existence of intramolecular Se···H–O hydrogen bonding in the solid and solution states have appeared in the literature,[11] intermolecular Se···H–O hydrogen bonding interactions have been reported in few prior cases.[12] In this article we report another example that shows intermolecular Se···H–O hydrogen bonding between *trans*-[*t*Bu(H)N(Se)P(μ-NCy)]$_2$ and H_2O in the solid state.

Results and Discussion

Synthesis of Bis(amido)-λ³-cyclodiphosphazanes

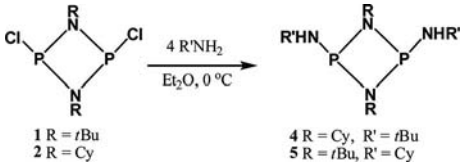
The reaction between PCl_3 and $CyNH_2$ with different stoichiometries was investigated in toluene at –78 °C (Scheme 2). The 1:3 stoichiometric reaction afforded the dichloro-λ³-cyclodiphosphazane, *cis*-[ClP(μ-NCy)]$_2$ (**2**), as the major product along with $CyNHPCl_2$, as indicated by the ^{31}P NMR spectroscopy. The ^{31}P NMR spectrum of the crude reaction mixture showed two singlets with the major singlet at δ = 218.6 ppm (63%), which was assigned to *cis*-[ClP(μ-NCy)]$_2$, and the upfield resonance at δ = 155.8 ppm (31%), which was due to $CyNHPCl_2$. Some unknown products in minor amounts (ca. 6%) were also observed as shown by the peaks near δ = 0 ppm. The pure dichloro derivative **2** was separated from the crude reaction mixture by vacuum distillation at 128 °C (0.3 Torr) and was readily recrystallized by cooling the hexane solution of **2** to –30 °C. Compound **2** is a colorless crystalline solid and is soluble in the common organic solvents, such as hexane, toluene, diethyl ether, dichloromethane, and THF. The modified synthetic procedure reported here for *cis*-[ClP(μ-NCy)]$_2$ is simple and quite efficient compared to that of the earlier report.[13] The 1:5 stoichiometric reaction between PCl_3 and $CyNH_2$ in toluene, which was performed at –78 °C and then heated under reflux, resulted in the formation of the bis(amido) derivative, *cis*-[Cy(H)NP(μ-NCy)]$_2$ (**3**). The ^{31}P NMR spectrum of **3** exhibits a single resonance at δ = 93.8 ppm, which is in the range of that previously reported for the bis(amido)-λ³-cyclodiphosphazane derivatives.[14,15] The dichloro derivative **2** was readily converted into the bis(amido) derivative **3** by treatment of **2** with four equivalents of cyclohexylamine in diethyl ether at 0 °C.

The bis(amido)-λ³-cyclodiphosphazane *cis*-[*t*Bu(H)NP(μ-NCy)]$_2$ (**4**) was obtained in good yield by the nucleophilic substitution reaction of *cis*-[ClP(μ-NCy)]$_2$ (**2**) with four equivalents of *t*BuNH$_2$ in Et_2O at 0 °C (Scheme 3). The bis(amido)cyclodiphosphazane *cis*-[Cy(H)NP(μ-N*t*Bu)]$_2$ (**5**), which has the identical chemical composition as that of **4**, was obtained in 95% yield by the reaction of



Scheme 2. The synthesis of the dichlorodiphosphazanes.

cis-[ClP(μ-N*t*Bu)]$_2$ (**1**) with four equivalents of cyclohexylamine under similar reaction conditions. The ^{31}P NMR spectra of **4** and **5** show single resonances at δ = 92.1 and 92.0 ppm, respectively. The ^{1}H NMR spectroscopy, FTIR spectroscopy, elemental analysis and mass spectrometry further support the proposed structures for the λ³-cyclodiphosphazane derivatives **2**–**5**.



Scheme 3. The synthesis of the bis(amido)cyclodisphosphazanes.

Synthesis of Bis(amido)-λ⁵-cyclodiphosphazanes

The reaction of the bis(amido)-λ³-cyclodiphosphazanes **3**–**5** with H_2O_2 in THF at –78 °C afforded the corresponding bis(oxo) derivatives **6**–**8** as crystalline solids. The ^{31}P NMR spectra for **6**–**8** exhibit single resonances at δ = –2.0, –3.2, and –2.2 ppm, respectively. The bis(sulfide) (**9**–**11**) and the bis(selenide) derivatives **12**–**14** were prepared by reacting the corresponding bis(amido)-λ³-diphosphazanes **3**–**5** with two equivalents of elemental sulfur or selenium in toluene under reflux conditions (Scheme 4). The bis(oxo) and bis(sulfide) derivatives are quite stable on exposure to air and moisture whereas the bis(selenide) derivatives are sensitive and need to be handled under inert conditions. The ^{31}P NMR spectra of the bis(sulfide) derivatives **9**–**11** exhibit single resonances at δ = 44.2, 41.0, and 43.4 ppm, respectively. The ^{31}P NMR spectrum of bis(selenide) **12** consists of a sharp singlet at δ = 35.4 ppm, superimposed on which are two approximate doublets (92:8 as per NMR intensity) corresponding to the ^{77}Se satellites arising from the isotopomer [CyN(H)P(Se)(μ-NCy)$_2$P(^{77}Se)N(H)Cy]. The satellite pattern is strictly the AA′ portion of an AA′X spin system [A, A′ = ^{31}P; X = ^{77}Se (I = 1/2, 7.6% abundance)] as a result of the magnetic nonequivalence of the phosphorus atoms. A $|^1J_{PSe}|$ (AX) coupling of 873 Hz and, similarly, a $|^2J_{PP'}|$ (AA′) coupling of 27 Hz was obtained from the satellite spectra for compound **12**. The compounds **13** and **14** exhibit a similar pattern in their ^{31}P NMR spec-

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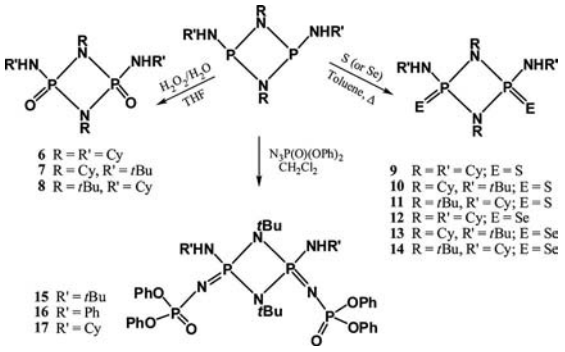
tra, however, they show a slightly lower $|^2J_{PP'}|$ coupling compared to that of **12**. The structures of bis(sulfide) **11** and bis(sele/nide) **12** and **13** were confirmed by single-crystal X-ray diffraction studies.



Scheme 4. The reactions of the bis(amido)-λ^3-cyclodisphosphazanes.

The Crystal and Molecular Structure for 11, 12, and 13

The perspective views for the molecular structures of compounds **11**–**13** are shown in Figures 1, 2, and 3, respectively. Relevant bond lengths and bond angles are listed in Table 1, whereas the crystal data and the details of the structural determinations are summarized in Table 3. In the molecular structures for the bis(sulfide) and bis(selenide) derivatives, *cis*-[Cy(H)N(S)P(μ-N*t*Bu)]$_2$ (**11**) and *cis*-[Cy(H)N(Se)P(μ-NCy)]$_2$ (**12**), respectively, both the two exocyclic nitrogen substituents and the two chalcogens (S or Se) are arranged in a *cis* configuration. In both of the compounds there is no imposed crystallographic symmetry but the corresponding bond lengths and angles are only slightly different. For example, the P1–S1 [1.927(1) Å] and P2–S2 [1.950(1) Å] bond lengths in **11** are in good agreement with those reported for the bis(amido)-λ^5-cyclodiphosphazane derivatives.[16] The crystal structure of the bis(selenide) derivative, *trans*-[*t*Bu(H)N(Se)P(μ-NCy)]$_2$ (**13**), shows that it adopts a *trans* conformation where the asymmetric unit consists of two different half molecules of **13** along with a water molecule. The crystal structures for several *trans* isomers for bis(sulfide) and bis(imine) derivatives of cyclodiphosphazanes have been reported,[17] but, to the best of our knowledge, there are no previously reported single-crystal X-ray structures that show a bis(selenide) derivative of cyclodiphosphazane that exists solely in the *trans* conformation. The recently reported cyclodiphosphazane derivative, [Cl(Se)P(μ-N*t*Bu)]$_2$, has been interpreted as a mixture of the *cis* and *trans* isomers in a 7:1 ratio.[18] Thus, the crystal structure for **13** is the first one reported for a pure *trans* bis(selenide)cyclodiphosphazane derivative. The bond lengths for both the *cis* and the *trans* isomers of the bis(selenides), **12** and **13**, are quite similar. However, in the *trans* isomer each P_2N_2 ring is strictly planar since each molecule possesses crystallographically-imposed centrosymmetry. In addition, the *ipso* carbon atom of the cyclohexyl group is essentially in the same plane, as indicated by the sum of the angles around N2 in **13**, which is 358.72(14)°. The corresponding sum of the angles around N1 in **11** is 355.96(11)°, whereas in **12** it is 346.68(13)°. This clearly indicated that in molecule **12** the four-membered P_2N_2 ring is highly puckered, which is supported by the dihedral angle between the two [PNN] planes (9.2° in **11** compared to 26.3° in **12**).

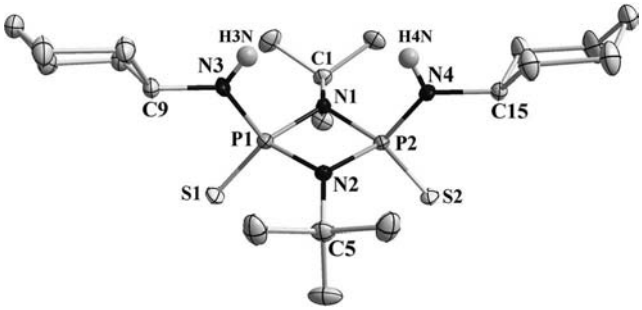


Figure 1. The thermal ellipsoid plot for **11** at the 50% probability level. The hydrogen atoms are omitted for clarity, except at N3 and N4.

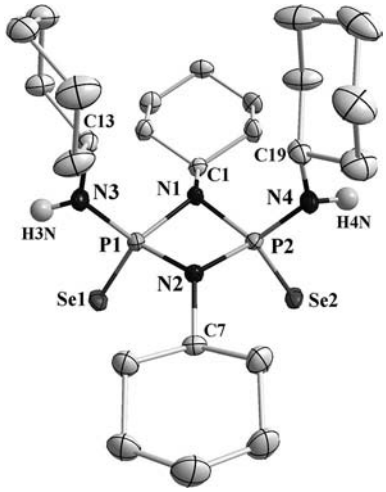


Figure 2. The thermal ellipsoid plot for **12** at the 50% probability level. The hydrogen atoms are omitted for clarity, except at N3 and N4.

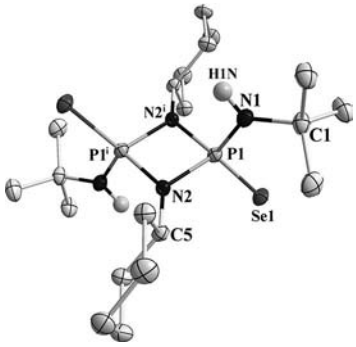


Figure 3. The thermal ellipsoid plot for **13** at the 50% probability level. The hydrogen atoms are omitted for clarity, except at N1.

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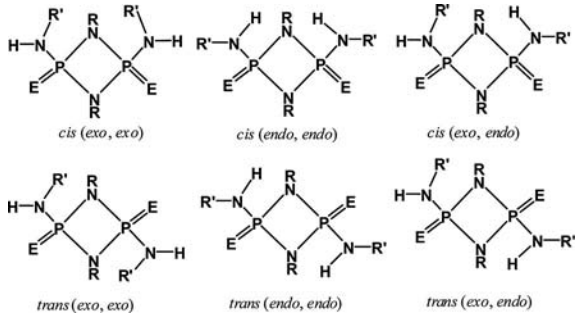
Table 1. The selected bond lengths [Å] and bond angles [°] for **11**, **12**, and **13**.

Bond lengths		Bond Angles	
11			
P1–S1	1.927(1)	S1–P1–N3	111.47(7)
P2–S2	1.950(1)	S2–P2–N4	109.82(6)
P1–N3	1.630(2)	S1–P1–N2	117.97(6)
P2–N4	1.619(2)	S2–P2–N2	119.24(6)
P1–N1	1.690(2)	N1–P1–N2	83.10(8)
P1–N2	1.692(2)	N1–P2–N2	83.33(9)
P2–N1	1.689(2)	P1–N1–P2	96.32(9)
P2–N2	1.685(2)	P1–N2–P2	96.41(9)
N1–C1	1.493(3)	P1–N1–C1	129.30(12)
N2–C5	1.483(3)	P2–N1–C1	130.34(13)
N3–C9	1.470(3)	P1–N2–C5	130.04(14)
N4–C15	1.473(3)	P2–N2–C5	130.82(14)
12			
P1–Se1	2.093(1)	N3–P1–Se1	111.56(7)
P2–Se2	2.088(1)	N4–P2–Se2	111.96(8)
P1–N3	1.615(2)	Se1–P1–N2	117.92(6)
P2–N4	1.618(3)	Se2–P2–N2	118.16(7)
P1–N1	1.689(3)	N1–P1–N2	83.27(10)
P1–N2	1.710(2)	N1–P2–N2	83.56(10)
P2–N1	1.696(2)	P1–N1–P2	94.35(11)
P2–N2	1.694(3)	P1–N2–P2	93.69(9)
N1–C1	1.482(3)	P1–N1–C1	127.04(14)
N2–C7	1.481(3)	P2–N1–C1	125.29(16)
N3–C13	1.469(3)	P1–N2–C7	125.10(14)
N4–C19	1.474(3)	P2–N2–C7	124.22(14)
13			
P1–Se1	2.096(2)	N1–P1–Se1	113.68(7)
P1–N1	1.627(2)	N2–P1–Se1	121.51(7)
P1–N2	1.675(2)	P1–N2–P1^{i}	97.21(11)
P1–N2^{i}	1.698(2)	P1–N2–C5	134.51(16)
		P1^{i}–N2–C5	127.00(15)
P2–Se2	2.105(1)	Se2–P2–N3	113.59(8)
P2–N3	1.619(2)	Se2–P2–N4	119.28(8)
P2–N4	1.674(2)	P2–N4–P2^{i}	97.77(12)
P2–N4^{i}	1.678(2)	P2–N4–C15	123.27(20)
		P2^{i}–N4–C15	138.9(2)
Se1···H2O–O	3.354(2)	Se1···H2O–O	173.00
Se2···H1O–O	3.368(2)	Se2···H1O–O	167.00
N1–H1N···O	2.992(2)	N1–H1N···O	172.00
N3–H3N···O	2.971(3)	N3–H3N···O	173.00

Three different conformational isomers are feasible for the *cis* isomer of a bis(amido)-λ⁵-cyclodiphosphazane with respect to the relative orientations of the exocyclic nitrogen substitutents. Similarly, three conformational isomers are possible for the *trans* isomer as depicted in Scheme 5. Interestingly, the bis(sulfide) derivative **11** showed an (*endo*,*endo*) arrangement of the substitutents in the solid state, whereas in **12** and **13** the exocyclic substituents were arranged in an (*exo*,*exo*) and an (*endo*,*endo*) fashion, respectively. It is worth noting that only the (*exo*,*endo*) isomer was observed in all of the structurally reported[17,19] chalcogenide derivatives of the type *cis*-[*t*BuNP(E)(NHR)]$_2$ (R = Ph, *t*Bu, E = S, Se). The (*endo*,*endo*) conformational arrangement was possibly favored in the solid state for **13** because of the presence of the lattice water molecules and the consequent formation of a linear hydrogen bonding network (Figure 4). The cyclohexyl groups that were present in all of the compounds adopted a stable chair conformation in the solid state.



Scheme 5. The possible conformational isomers for the bis(amido)-λ⁵-cyclodisphosphazanes.

We had hoped to assess the possible effect of no water molecules in the lattice on the structure of **13**. However, all attempts at growing X-ray quality single crystals of **13** without water were unsuccessful. We also tried to crystallize **12** and **14** in the presence of a small amount of H_2O using various organic solvents. However, we observed either no change in the obtained crystals or the formation of [*t*BuNH$_3$][H$_2$PO$_3$] (Figure 5), which presumably formed by means of the hydrolysis of the P–N bonds in the cyclodiphosphazane.

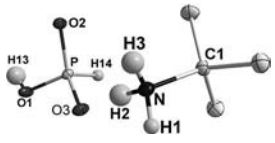


Figure 5. The thermal ellipsoid plot for [*t*BuNH$_3$][H$_2$PO$_3$] at the 50% probability level.

Synthesis of Phosphinimine Derivatives

The Staudinger reaction of the bis(amido)-λ³-cyclodiphosphazanes, *cis*-[R(H)NP(μ-N*t*Bu)]$_2$ (R = *t*Bu, Ph, Cy), with two equivalents of phosphoryl azide [N$_3$P(O)(OPh)$_2$] in CH_2Cl_2 at –78 °C resulted in the formation of bis(phos-

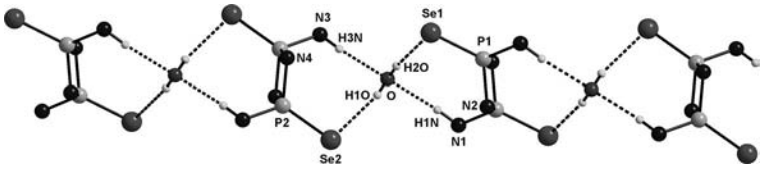


Figure 4. The hydrogen bonding in **13**. The substituents on N and P have been removed for clarity.

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phorylimine)-λ^5-cyclodiphosphazane derivatives of the type *cis*-{R(H)N[$(PhO)_2$(O)PN]P(μ-N*t*Bu)}$_2$ (**15–17**) in quantitative yield. All of the three compounds were air-stable, white crystalline solids. The ^{31}P NMR spectra for the compounds **15**–**17** appeared as AB quartets due to the close chemical shift values for the P=N center of the λ^5-cyclodiphosphazane and the P(O)$(OPh)_2$ groups. The ^{1}H NMR, the mass spectra, and the elemental analysis data were consistent with the proposed structures. The structure of compound **15** was confirmed by a single-crystal X-ray structure determination.

The Crystal and Molecular Structure for 15

The X-ray quality single-crystals for **15** were obtained by leaving a warm acetonitrile solution of **15** at room temperature for a day. The structure for *cis*-{*t*Bu(H)N[$(PhO)_2$(O)-PN]P(μ-N*t*Bu)}$_2$ (**15**) with the atom numbering scheme is shown in Figure 6. The selected bond angles and bond lengths for **15** are presented in Table 2. The compound maintains the *cis* arrangement of the two NH*t*Bu groups above the P_2N_2 plane, as well as the phosphoryl imine substituent [NP(O)$(OPh)_2$] below the heterocycle. In molecule **15**, the P–N*endo* bonds are longer than the P–N*exo* and P=N*exo* bonds. The P1–N3 [1.586(6) Å] and P2–N5 [1.605(6) Å] bond lengths are slightly shorter than that of bis(amido)-λ^3-cyclodiphosphazane, *cis*-[*t*Bu(H)NP(μ-N*t*Bu)]$_2$ [1.664(2) Å], which may be due to the relatively larger multiple bond character in the latter. The P=N distances [P1–N4 1.540(5) Å, P2–N6 1.510(8) Å] are comparable with those of the reported[20] imine derivatives of λ^5-cyclodiphosphazanes. The P1–N4–P3 bond angle is 141.92° whereas the P2–N6–P4 angle is 169.21°. This indicated that one of the exocyclic P=N–P moieties is nearly linear while the another one is bent. The water molecule present in the crystal structure of **15** generated an extended hydrogen bonding network that involved the exocyclic NH proton and the phosphoryl group oxygen of an adjacent molecule (Figure 7).

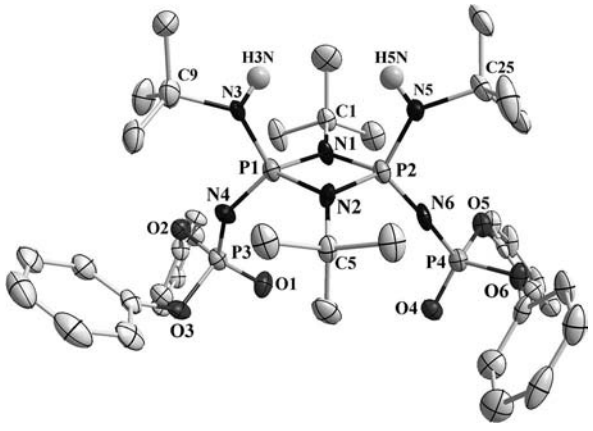

Figure 6. The thermal ellipsoid plot for **15** at the 50% probability level. The hydrogen atoms are omitted for clarity, except at N3 and N5.

Table 2. The selected bond lengths [Å] and bond angles [°] for **15**.

Bond lengths		Bond Angles	
P1–N3	1.586(6)	P1–N4–P3	141.9(3)
P2–N5	1.605(6)	P2–N6–P4	169.2(4)
P1–N4	1.540(5)	N4–P1–N3	108.6(3)
P2–N6	1.510(8)	N6–P2–N5	112.2(3)
P3–N4	1.563(5)	N4–P1–N2	118.0(3)
P4–N6	1.562(7)	N6–P2–N2	116.6(3)
P1–N1	1.675(4)	N4–P3–O1	122.6(3)
P1–N2	1.673(5)	N6–P4–O4	120.1(3)
P2–N1	1.685(7)	N1–P1–N2	83.9(3)
P2–N2	1.675(4)	N1–P2–N2	83.6(2)
N1–C1	1.494(9)	P1–N1–P2	95.9(3)
N2–C5	1.490(8)	P1–N2–P2	96.4(2)
N3–C9	1.499(9)	P1–N1–C1	132.4(5)
N5–C25	1.498(8)	P2–N1–C1	129.4(4)
P3–O1	1.458(6)	P1–N2–C5	129.6(4)
P4–O4	1.455(5)	P2–N2–C5	129.5(4)
P3–O2	1.613(5)	P1–N3–C9	133.6(4)
P3–O3	1.596(5)	P2–N5–C25	137.1(6)
P4–O5	1.604(4)	O7–H1W···O1	169.00
P4–O6	1.606(5)	O7–H2W···O4	169.00
O7–H1W···O1	2.638(7)	N3–H3N···O7	123.00
O7–H2W···O4	2.666(6)	N5–H5N···O7	155.00
N3–H3N···O7	2.903(6)		
N5–H5N···O7	2.796(8)		

Conclusions

The reaction of cyclohexylamine with PCl_3 afforded either the bis(chloro) or the bis(amido)-λ^3-cyclodiphosphazanes derivatives depending on the reactant ratios. These homo- and hetero-substituted bis(amido)-λ^3-cyclodiphosphazanes were highly soluble in the common organic solvents and could serve as useful starting compounds to make new cyclodiphosphazane derivatives. The first crystal structure for a pure *trans*-cyclodiphosphazane bis(selenide) isomer was established. Intermolecular Se···H–O hydrogen bonding was observed, which favored the formation of a 1D linear network in the solid. The reaction of phosphoryl azide with cyclodiphosphazane gave the imine derivative in

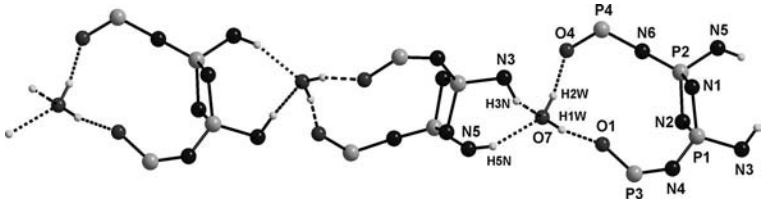

Figure 7. The hydrogen bonding in **15**. The subsituents on P and N are removed for clarity.

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good yield without changing the *cis* conformation of the P_2N_2 ring. The presence of a water molecule in the crystal lattice leads to a linear 1D hydrogen-bonded structure.

Experimental Section

General Procedures and Materials: All of the manipulations were performed under rigorously anaerobic conditions by using high vacuum manifolds and Schlenk techniques. All of the solvents were purified by conventional procedures and distilled prior to use.[21] The compounds *cis*-[ClP(μ-N*t*Bu)]$_2$ (**1**),[1e] *cis*-[*t*Bu(H)NP(μ-N*t*Bu)]$_2$ (**1a**),[14] and *cis*-[Ph(H)NP(μ-N*t*Bu)]$_2$ (**1b**)[15] were prepared according to the published procedures. PCl_3, $CyNH_2$, *t*$BuNH_2$, H_2O_2 (33% in H_2O), sulfur, selenium, and $N_3P(O)(OPh)_2$ were purchased from commercial sources and were purified prior to use by the conventional methods.

Instrumentation: The ^1H and $^{31}P\{^1H\}$ NMR (δ in ppm) spectra were recorded with Varian 300 or 400 Mercury Plus spectrometers that were operated at the appropriate frequencies. TMS and 85% H_3PO_4 were used as the internal and external references, respectively. The IR spectra were recorded as KBr discs with a Nicolet Impact 400 FTIR instrument. The microanalyses were performed with a Carlo Erba Model 1112 elemental analyzer. The mass spectrometry experiments were carried out with a Waters Q-Tof micro-YA-105 instrument. The melting points were recorded in capillary tubes and are uncorrected.

***Cis*-[ClP(μ-NCy)]$_2$ (2):** A solution of cyclohexylamine (34.08 g, 40 mL, 0.342 mol) in toluene (100 mL) was added dropwise to a well-stirred solution of PCl_3 (15.74 g, 10 mL, 0.114 mol) in toluene (400 mL) at –78 °C. After the completion of the addition, the reaction mixture was stirred at this temperature for 4 h and then heated under reflux for a further 4 h. The reaction mixture was then brought to room temperature and filtered to remove the amine hydrochloride. The filtrate was concentrated under reduced pressure to afford the product as a pasty white solid, which was then purified by vacuum distillation. The minor product, $PCl_2(NHCy)$, was distilled out at 70 °C (0.3 Torr), whereas the product **2** distilled out at 128 °C (0.3 Torr); yield 46% (8.57 g, 0.026 mol); m.p. 60–62 °C. ^1H NMR (300 MHz, $CDCl_3$): δ = 2.13–1.13 (m, 22 H, *Cy*) ppm. $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): δ = 218.6 (s) ppm. $C_{12}H_{22}Cl_2N_2P_2$ (327.17): calcd. C 44.05, H 6.78, N 8.56; found C 43.97, H 6.62, N 8.58. MS (EI): *m*/*z* = 328.07 [M + 1].

***cis*-[Cy(H)NP(μ-NCy)]$_2$ (3). Method A:** A solution of PCl_3 (7.87 g, 5 mL, 0.057 mol) in toluene (30 mL) was added dropwise to a solution of cyclohexylamine (28.98 g, 33.5 mL, 0.292 mol) in toluene (300 mL) at –78 °C over 1 h. The reaction mixture was heated under reflux for 5 h and then cooled to room temperature. Cyclohexylamine hydrochloride was removed by filtration through a frit containing an activated celite bed. The reaction mixture was concentrated to 20 mL under reduced pressure and stored at –30 °C for a day to yield the analytically pure colorless crystals of **3**; yield 83% (10.64 g, 0.023 mol).

Method B: A solution of cyclohexylamine (3.84 g, 38.7 mmol) in diethyl ether (25 mL) was added dropwise to a well-stirred solution of *cis*-[ClP(μ-NCy)]$_2$ (**2**) (3.17 g, 9.69 mmol) in diethyl ether (100 mL) at 0 °C. The reaction mixture was further stirred for 14 h at room temperature. The amine hydrochloride was filtered off, the filtrate was concentrated to 15 mL under reduced pressure, and stored at –30 °C for a day to obtain a colorless crystalline product; yield 88% (3.85 g, 8.52 mmol); m.p. 132–134 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 3.57 (br. s, 2 H, N*H*), 2.27–1.12 (m, 44 H, *Cy*) ppm. $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): δ = 93.8 (s) ppm. FTIR (KBr): $\tilde{\nu}$ = 3354 [ν(N–H)] cm^{-1}. $C_{24}H_{46}N_4P_2$ (452.59): calcd. C 63.68, H 10.24, N 12.37; found C 63.64, H 10.26, N 12.34. MS (EI): *m*/*z* = 453.29 [M + 1].

***cis*-[*t*Bu(H)NP(μ-NCy)]$_2$ (4):** A solution of *t*$BuNH_2$ (1.99 g, 27.13 mmol) in diethyl ether (10 mL) was added dropwise to a stirred ice-cold solution of *cis*-[ClP(μ-NCy)]$_2$ (2.22 g, 6.78 mmol) in diethyl ether (50 mL). After the completion of the addition, the reaction mixture was stirred at room temperature for 18 h. The precipitated amine hydrochloride was removed by filtration; the filtrate was concentrated (15 mL), and stored at –30 °C for a day to obtain the crystalline product; yield 90% (2.45 g, 6.10 mmol); m.p. 128–130 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 3.28 (s, 2 H, N*H*), 2.09–1.14 (m, 22 H, *Cy*), 1.38 (s, 18 H, *tBu*) ppm. $^{31}P\{^1H\}$ NMR (161 MHz, $CDCl_3$): δ = 92.1 (s) ppm. FTIR (KBr): $\tilde{\nu}$ = 3327 [ν(N–H)] cm^{-1}. $C_{20}H_{42}N_4P_2$ (400.52): calcd. C 59.97, H 10.56, N 13.98; found C 60.05, H 10.48, N 13.84. MS (EI): *m*/*z* = 401.31 [M + 1].

***cis*-[Cy(H)NP(μ-N*t*Bu)]$_2$ (5):** A procedure analogous to that of **4** was followed. *cis*-[ClP(μ-N*t*Bu)]$_2$ (**1**) (1.79 g, 6.52 mmol) and cyclohexylamine (2.59 g, 26.1 mmol) were used; yield 95% (2.48 g, 6.21 mmol); m.p. 124–126 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 3.46 (br. s, 2 H, N*H*), 1.95–1.17 (m, 22 H, *Cy*), 1.36 (s, 18 H, *tBu*) ppm. $^{31}P\{^1H\}$ NMR (161 MHz, $CDCl_3$): δ = 92.0 (s) ppm. FTIR (KBr): $\tilde{\nu}$ = 3302 [ν(N–H)] cm^{-1}. $C_{20}H_{42}N_4P_2$ (400.52): calcd. C 59.97, H 10.56, N 13.98; found C 59.64, H 10.51, N 13.84. MS (EI): *m*/*z* = 401.24 [M + 1].

***cis*-[Cy(H)N(O)P(μ-NCy)]$_2$ (6):** A solution of H_2O_2 (33% in H_2O) (2.3 mL, 10.25 mmol) in THF (15 mL) was added dropwise to a solution of *cis*-[Cy(H)NP(μ-NCy)]$_2$ (**3**) (2.32 g, 5.12 mmol) in THF (30 mL) at –78 °C. The reaction mixture was warmed to room temperature and stirred for 4 h. The addition of hexane (10 mL) to the reaction mixture precipitated the product as a colorless solid; yield 88% (2.17 g, 4.48 mmol); m.p. $<$ 260 °C. ^1H NMR (300 MHz, $CDCl_3$): δ = 3.13 (br. s, 2 H, N*H*), 1.19–2.14 (m, 44 H, *Cy*) ppm. $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): δ = –2.0 (s) ppm. FTIR (KBr): $\tilde{\nu}$ = 3193 [ν(N–H)], 1063 [ν(P=O)] cm^{-1}. $C_{24}H_{46}N_4O_2P_2$ (484.59): calcd. C 59.48, H 9.56, N 11.56; found C 59.37, H 10.04, N 11.51. MS (EI): *m*/*z* = 485.28 [M + 1].

***cis*-[*t*Bu(H)N(O)P(μ-NCy)]$_2$ (7):** The compound was synthesized analogously to compound **6**. *cis*-[*t*Bu(H)NP(μ-NCy)]$_2$ (**4**) (0.429 g, 1.072 mmol) and H_2O_2 (0.27 mL, 2.14 mmol) were used; yield 87% (0.403 g, 0.93 mmol); m.p. $<$ 260 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 3.15 (br. s, 2 H, N*H*), 2.46–1.14 (m, 22 H, *Cy*), 1.36 (s, 18 H, *tBu*) ppm. $^{31}P\{^1H\}$ NMR (161 MHz, $CDCl_3$): δ = –3.2 (s) ppm. FTIR (KBr): $\tilde{\nu}$ = 3175 [ν(N–H)], 1089 [ν(P=O)] cm^{-1}. $C_{20}H_{42}N_4O_2P_2$ (432.52): calcd. C 55.54, H 9.78, N 12.95; found C 55.64, H 9.76, N 12.81. MS (EI): *m*/*z* = 433.34 [M + 1].

***cis*-[Cy(H)N(O)P(μ-N*t*Bu)]$_2$ (8):** The compound was synthesized analogously to compound **6**. *cis*-[Cy(H)NP(μ-N*t*Bu)]$_2$ (**5**) (0.709 g, 1.77 mmol) and H_2O_2 (0.41 mL, 3.54 mmol) were used; yield 93% (0.71 g, 1.64 mmol); m.p. $<$ 260 °C. ^1H NMR (300 MHz, $CDCl_3$): δ = 3.49 (br. s, 2 H, N*H*), 2.01–1.17 (m, 22 H, *Cy*), 1.42 (s, 18 H, *tBu*) ppm. $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): δ = –2.2 (s) ppm. FTIR (KBr): $\tilde{\nu}$ = 3164 [ν(N–H)], 1091 [ν(P=O)] cm^{-1}. $C_{20}H_{42}N_4O_2P_2$ (432.52): calcd. C 55.53, H 9.78, N 12.95; found C 55.57, H 10.07, N 12.83. MS (EI): *m*/*z* = 433.30 [M + 1].

***cis*-[Cy(H)N(S)P(μ-NCy)]$_2$ (9):** A mixture of *cis*-[Cy(H)NP(μ-NCy)]$_2$ (**3**) (2.64 g, 5.83 mmol) and sulfur (0.37 g, 11.6 mmol) in toluene (50 mL) was heated under reflux for 12 h. The reaction mixture was cooled to room temperature and filtered through activated celite. The toluene was removed under reduced pressure. The

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residue was washed with hexane (2 × 15 mL) and dried under vacuum to yield the product as a colorless solid; yield 80% (2.40 g, 4.65 mmol); m.p. 210–212 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.40 (s, 2 H, N*H*), 2.39–1.15 (m, 44 H, *Cy*) ppm. $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): δ = 44.2 (s) ppm. FTIR (KBr): $\tilde{\nu}$ = 3238 [ν(N–H)], 942 [ν(P=S)] cm^{-1}. $C_{24}H_{46}N_4P_2S_2$ (516.72): calcd. C 55.78, H 8.97, N 10.84, S 12.41; found C 55.92, H 9.07, N 10.81, S 12.86. MS (EI): *m*/*z* = 517.34 [M + 1].

***cis*-[*t*Bu(H)N(S)P(μ-NCy)]$_2$ (10):** The compound was synthesized analogously to compound **9**. *cis*-[*t*Bu(H)NP(μ-NCy)]$_2$ (**4**) (0.50 g, 1.25 mmol) and sulfur (81.0 mg, 2.51 mmol) were heated under reflux in toluene (15 mL); yield 78% (0.46 g, 0.98 mmol); m.p. 178–180 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.47 (s, 2 H, N*H*), 2.47–1.17 (m, 22 H, *Cy*), 1.40 (s, 18 H, *tBu*) ppm. $^{31}P\{^1H\}$ NMR (161 MHz, $CDCl_3$): δ = 41.0 (s) ppm. FTIR (KBr): $\tilde{\nu}$ = 3226 [ν(N–H)], 914 [ν(P=S)] cm^{-1}. $C_{20}H_{42}N_4P_2S_2$ (464.65): calcd. C 51.70, H 9.11, N 12.06, S 13.80; found C 51.63, H 9.21, N 11.98, S 14.01. MS (EI): *m*/*z* = 465.91 [M + 1].

***cis*-[Cy(H)N(S)P(μ-N*t*Bu)]$_2$ (11):** The compound was synthesized analogously to compound **9**. *cis*-[Cy(H)NP(μ-N*t*Bu)]$_2$ (**5**) (0.36 g, 0.90 mmol) and sulfur (57.2 mg, 1.80 mmol) were used; yield 86% (0.36 g, 0.77 mmol); m.p. 232–234 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.32 (s, 2 H, N*H*), 2.18–1.15 (m, 22 H, *Cy*), 1.57 (s, 18 H, *tBu*) ppm. $^{31}P\{^1H\}$ NMR (161 MHz, $CDCl_3$): δ = 43.4 (s) ppm. FTIR (KBr): $\tilde{\nu}$ = 3276 [ν(N–H)], 910 [ν(P=S)] cm^{-1}. $C_{20}H_{42}N_4P_2S_2$ (464.65): calcd. C 51.69, H 9.11, N 12.05, S 13.80; found C 51.57, H 9.10, N 12.18, S 14.26. MS (EI): *m*/*z* = 465.69 [M + 1].

***cis*-[Cy(H)N(Se)P(μ-NCy)]$_2$ (12):** A mixture of *cis*-[Cy(H)NP(μ-NCy)]$_2$ (**3**) (1.49 g, 3.32 mmol) and selenium powder (0.52 g, 6.64 mmol) was heated in toluene (30 mL) at 120 °C for 12 h. The reaction mixture was cooled to room temperature and the unreacted selenium was removed by filtration. The toluene was then removed under reduced pressure, the residue was washed with petroleum ether (2× 10 mL), redissolved in a CH_2Cl_2/petroleum ether (1:1) mixture, and then stored at –30 °C for a day to obtain a crystalline product; yield 63% (1.27 g, 2.08 mmol); m.p. 230–232 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.28 (br. s, 2 H, N*H*), 2.50–1.12 (m, 44 H, *Cy*) ppm. $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): δ = 35.4 (s, $^1J_{PSe}$ = 873 Hz, $^2J_{PP}$ = 27 Hz) ppm. FTIR (KBr): $\tilde{\nu}$ = 3223 [ν(N–H)], 577 [ν(P=Se)] cm^{-1}. $C_{24}H_{46}N_4P_2Se_2$ (610.51): calcd. C 47.22, H 7.59, N 9.18; found C 47.19, H 7.41, N 9.09. MS (EI): *m*/*z* = 633.10 [M + Na].

***trans*-[*t*Bu(H)N(Se)P(μ-NCy)]$_2$ (13):** The compound was synthesized analogously to compound **12**. *cis*-[*t*Bu(H)NP(μ-NCy)]$_2$ (**4**) (0.74 g, 1.84 mmol) and selenium (0.29 g, 3.67 mmol) were used; yield 66% (0.672 g, 1.20 mmol); m.p. 182–184 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.38 (br. s, 2 H, N*H*), 2.57–1.19 (m, 22 H, *Cy*), 1.46 (s, 18 H, *tBu*) ppm. $^{31}P\{^1H\}$ NMR (161 MHz, $CDCl_3$): δ = 32.7 (s, $^1J_{PSe}$ = 875 Hz, $^2J_{PP}$ = 23 Hz) ppm. FTIR (KBr): $\tilde{\nu}$ = 3204 [ν(N-H)], 575 [ν(P=Se)] cm^{-1}. $C_{20}H_{42}N_4P_2Se_2$ (558.44): calcd. C 43.02, H 7.58, N 10.03; found C 43.11, H 7.59, N 9.92. MS (EI): *m*/*z* = 561.23 [M + 1].

***cis*-[Cy(H)N(Se)P(μ-N*t*Bu)]$_2$ (14):** The compound was synthesized analogously to compound **12**. *cis*-[Cy(H)NP(μ-N*t*Bu)]$_2$ (**5**) (0.424 g, 1.05 mmol) and selenium (0.18 g, 2.11 mmol) were used; yield 77% (0.45 g, 0.81 mmol); m.p. 116–118 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.37 (br. s, 2 H, N*H*), 1.18–2.02 (m, 22 H, *Cy*), 1.58 (s, 18 H, *tBu*) ppm. $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): δ = 31.6 (s, $^1J_{PSe}$ = 878 Hz, $^2J_{PP}$ = 19 Hz) ppm. FTIR (KBr): $\tilde{\nu}$ = 3262 [ν(N–H)], 518 [ν(P=Se)] cm^{-1}. $C_{20}H_{42}N_4P_2Se_2$ (558.44): calcd. C 43.02, H 7.58, N 10.03; found C 43.18, H 7.52, N 9.73. MS (EI): *m*/*z* = 561.16 [M + 1].

***cis*-{*t*Bu(H)N[(PhO)$_2$(O)PN]P(μ-N*t*Bu)}$_2$ (15):** A dichloromethane (5 mL) solution of $N_3P(O)(OPh)_2$ (1.52 g, 5.53 mmol) was added dropwise to a solution of *cis*-[*t*Bu(H)NP(μ-N*t*Bu)]$_2$ (**1a**) (0.96 g, 2.76 mmol) in dichloromethane (15 mL) at –78 °C. After the addition, the reaction mixture was slowly warmed to room temperature and stirred for a further 8 h. The solvent was removed under reduced pressure, the residue was washed with petroleum ether (2× 5 mL), redissolved in hot acetonitrile, and stored at room temperature for a day to afford **15** as colorless crystals; yield 79% (1.84 g, 2.19 mmol); m.p. 160–162 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.31–7.05 (m, 20 H, *Ph*), 3.99 (br. s, 2 H, N*H*), 1.44 (s, 18 H, *tBu*), 1.37 (s, 18 H, *tBu*) ppm. $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): δ = –15.1, –16.9 (AB quartet, $|J_{ab}|$ = 65 Hz) ppm. FTIR (KBr): $\tilde{\nu}$ = 3202 [ν(N–H)], 1072 [ν(P=O)] cm^{-1}. $C_{40}H_{58}N_6O_6P_4$ (842.82): calcd. C 57.00, H 6.93, N 9.97; found C 56.92, H 6.81, N 9.95. MS (EI): *m*/*z* = 843.39 [M + 1].

***cis*-{Ph(H)N[(PhO)$_2$(O)PN]P(μ-N*t*Bu)}$_2$ (16):** The compound was synthesized analogously to compound **15**. *cis*-[Ph(H)NP(μ-N*t*Bu)]$_2$ (**1b**) (0.28 g, 0.73 mmol) and $N_3P(O)(OPh)_2$ (0.41 g, 1.47 mmol) were used; yield 62% (0.39 g, 0.45 mmol); m.p. 168–172 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.34–7.05 (m, 30 H, *Ph*), 3.48 (br. s, 2 H, N*H*), 1.27 (s, 18 H, *tBu*) ppm. $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): δ = –10.1, –10.3 (AB quartet, $|J_{ab}|$ = 18.3 Hz) ppm. FTIR (KBr): $\tilde{\nu}$ = 3151 [ν(N–H)], 1091 [ν(P=O)] cm^{-1}. $C_{44}H_{50}N_6O_6P_4$ (882.80): calcd. C 59.86, H 5.70, N 9.51; found C 59.71, H 5.77, N 9.44. MS (EI): *m*/*z* = 883.23 [M + 1].

***cis*-{Cy(H)N[(PhO)$_2$(O)PN]P(μ-N*t*Bu)}$_2$ (17):** The compound was synthesized analogously to compound **15**. *cis*-[Cy(H)NP(μ-N*t*Bu)]$_2$ (**5**) (0.45 g, 1.1 mmol) and $N_3P(O)(OPh)_2$ (0.61 g, 2.2 mmol) were used; yield 75% (0.73 g, 0.82 mmol); m.p. 185–187 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.41–7.09 (m, 20 H, *Ph*), 3.14 (br. s, 2 H, N*H*), 2.55–1.17 (m, 22 H, *Cy*), 1.29 (s, 18 H, *tBu*) ppm. $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): δ = –5.7, –9.7 (AB quartet, $|J_{ab}|$ = 60 Hz) ppm. FTIR (KBr): $\tilde{\nu}$ = 3203 [ν(N–H)], 1084 [ν(P=O)] cm^{-1}. $C_{44}H_{62}N_6O_6P_4$ (894.89): calcd. C 59.05, H 6.98, N 9.39; found C 59.21, H 6.87, N 9.42. MS (EI): *m*/*z* = 895.46 [M + 1].

Single-Crystal X-ray Crystallography: See also Table 3; crystals of **11**, **12**, **13**, and **15** were mounted in a CryoLoop™ with a drop of Paratone oil and placed in the cold nitrogen stream of the Kryoflex™ attachment of the Bruker APEX CCD diffractometer. For each, a full sphere of data was collected by using 606 scans in ω (0.3° per scan) at ϕ = 0, 120, and 240° with the SMART software package.[22] The raw data were reduced to F^2 values by using the SAINT+[23] software and global refinements of the unit cell parameters were performed by employing 3396–8074 reflections that were chosen from the full data set. The multiple measurements of equivalent reflections provided the basis for the empirical absorption correction as well as a correction for any crystal deterioration during the data collection (SADABS).[24] The structures of **11** and **12** were solved by the Patterson methods, while the remaining structures were solved by direct methods. All of the structures were refined by full-matrix least-squares procedures using the SHELXTL program package.[25] The hydrogen atoms that were attached to carbon were placed in the calculated positions [C–H 0.95 Å (aromatic rings) or 0.98 Å (methyl groups)] and were included as riding contributions with the isotropic displacement parameters of 1.2 (aromatic rings) or 1.5 (methyl groups) times those of the attached non-hydrogen atoms. The hydrogen atoms that were attached to nitrogen were placed in positions that were derived from difference

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Table 3. The crystallographic information for compounds **11**, **12**, **13**, and **15**.

	11	**12**	**13**·H_2O	**15**·H_2O	[*t*BuNH_3][H_2PO_3]
Formula	$C_{20}H_{42}N_4P_2S_2$	$C_{24}H_{46}N_4P_2Se_2$	$C_{20}H_{44}N_4OP_2Se_2$	$C_{40}H_{60}N_6O_7P_4$	$C_4H_{14}NO_3P$
Fw [g mol^{-1}]	464.64	610.51	576.45	860.82	155.13
Crystal system	monoclinic	monoclinic	triclinic	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/n$	$P\bar{1}$	Cc	$P2_1/n$
a [Å]	10.5354(7)	15.321(3)	10.3525(7)	22.608(4)	7.4695(6)
b [Å]	23.815(2)	14.190(3)	11.3643(8)	13.431(3)	6.540(6)
c [Å]	11.4697(7)	15.421(3)	12.7216(9)	16.966(3)	16.160(1)
α [°]	90	90	106.684(1)	90	90
β [°]	115.290(1)	119.184(3)	105.258(1)	121.804(3)	93.360(1)
γ [°]	90	90	99.912(1)	90	90
V [Å^3]	2601.9(3)	2927.0(10)	1332.54(16)	4378.2(15)	788.07(11)
Z	4	4	2	4	4
ρ_{calc} [g cm^{-3}]	1.186	1.385	1.415	1.306	1.308
μ(Mo-K_a) [mm^{-1}]	0.341	2.654	2.896	0.227	0.295
F (000)	1008	1264	588	1832	336
Crystal size [mm^3]	0.02 × 0.15 × 0.18	0.01 × 0.14 × 0.19	0.07 × 0.13 × 0.22	0.04 × 0.07 × 0.18	0.10 × 0.17 × 0.22
T [K]	100	150	293	100	100
2*θ* range [°]	1.7 to 27.1	1.5 to 28.3	2.1 to 28.3	1.9 to 24.8	2.5 to 28.3
Total reflections	22243	25734	23665	15051	6638
Independent refl.	5750 [R_{int} = 0.049]	7007 [R_{int} = 0.041]	6533 [R_{int} = 0.034]	7233 [R_{int} = 0.096]	1877 [R_{int} = 0.023]
R_1[a]	0.0419	0.0338	0.0364	0.0624	0.0315
wR_2[b]	0.1030	0.0786	0.0933	0.1391	0.0849
GOF (F^2)	1.02	1.01	1.04	0.99	1.08

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR_2 = \{[\Sigma w(F_o^2 - F_c^2)/\Sigma w(F_o^2)^2]\}^{1/2}$ $w = 1/[\sigma^2(F_o^2) + (xP)^2]$ where $P = (F_o^2 + 2F_c^2)/3$.

maps and were included as riding contributions with the isotropic displacement parameters of 1.2 times those of the attached atom.

CCDC-795653 (for **11**), -795654 (for **12**), -795655 (for **13**), and -795656 (for **15**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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