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Synthesis of Bis- and Tris(3-*H*-1,3-azaphospholo)benzenes

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ABSTRACT: *The previously developed intramolecular cyclocondensation of C-phosphanyl(N-aryl) formamidines into 3-H-1,3-benzazaphospholes has been successfully extended to 1,3-diaminobenzene and 1,3,5-triaminobenzene. Its condensation presents the way to tricyclic and tetracyclic azaphospholes. Their structures were confirmed by spectroscopic methods and key tricyclic and tetracyclic compounds were further characterized by single crystal X-ray diffraction.*
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INTRODUCTION

Presently, the number of synthetic routes to phosphorus heterocycles is considerably limited compared with the multitude of methods for the preparation of their oxygen and nitrogen analogues. Among phosphorus heterocycles, fused azaphospholes are of considerable interest [1, 2]. Poly(3-*H*-1, 3-azaphospholo)benzenes are supposed to be highly symmetrical compounds that might be useful starting materials for metal-organic frameworks [3] and symmetrical tripod scaffold for the construction of receptors [4]. Azaphospholes and related annulated compounds have been the subject of a few studies concerning their synthesis methods, structural features, and metal coordination properties [1, 2]. It should be noted that 1,3-azaphosphole can exist in two tautomeric forms, with either a σ^2,λ^3-phosphorus (**I**) or a σ^3,λ^3-phosphorus (**II**) (Fig. 1).

3*H*-Azaphospholes lack the conjugation between the phosphorus lone pair and the rest of the π system because of the pyramidal structure of σ^3,λ^3-phosphorus [5]. A general synthetic approach to 3*H*-1,3-benzazaphospholes has only recently been reported. The starting *C*-phosphanyl(*N*-aryl)formamidines prepared using a diverse set of anilines have been shown to undergo cyclization yielding 3*H*-1,3-benzazaphospholes. The rate of the cyclization has been shown to depend on the benzene ring substituent electron-donating efficiency. At the same time, the method tolerates various substituents [6]. In this contribution, we describe the extension of the method to 1,3-diaminobenzene and 1,3,5-triaminobenzene to prepare polycyclic 3*H*-1,3-benzazaphospholes.

RESULTS AND DISCUSSION

First, we have investigated the reaction with 1,3-diaminobenzene. Unlike 1,2-diaminobenzene, 1,3-diaminobenzene was readily phosphorylated with a twofold amount of *N*,*N*-dimethyl-*P*-(trichloromethyl)phosphonamidous chloride at both amino groups affording trivalent derivative. It was not isolated as an individual compound,

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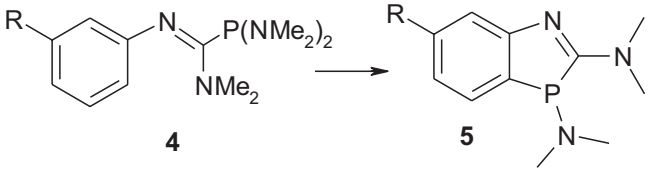
FIGURE 1 Tautomeric forms of azaphospholes.



SCHEME 2 Synthesis of substituted benzazaphospholes **5**.

but it was characterized by ^{31}P nuclear magnetic resonance (NMR) spectroscopy (δ_p 80 ppm). Then the compound was oxidized with selenium to the pentavalent derivative **2** as a mixture of diastereomers. Although the mixture was separated by chromatography into individual diastereomers, their absolute configurations were not assigned. Upon treatment with an excess of dimethylamine at room temperature in a sealed vial, the mixture of diastereomers **2** was converted into a stable crystalline pentavalent *C*-phosphorylated formamidine **3** in high yield (Scheme 1).

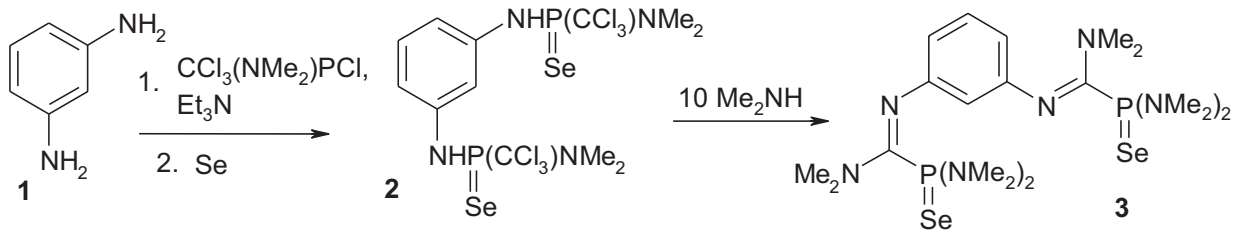
In our previous work, we showed that the cyclization of *C*-phosphorylated *N,N*-dimethyl-N′-arylformamidines critically depends on the position and electron-donating capability of substituents at the aryl ring (Scheme 2). The cyclization proceeds with the elimination of dimethylamine and its mechanism was described in detail [6b]. Electron-donating substituents at the meta position promoted cyclization the best. For R = Me_2N, compound **4** was not isolated as it spontaneously underwent cyclization to give benzazaphosphole **5** (Scheme 2). The compounds **4** bearing less electron-donating substituents are rather stable.

It was expected that the reduction of pentavalent compound **3** with two equivalents of hexamethylphosphorus triamide would afford trivalent *C*-phosphorylated formamidine **6**. As electron-donor properties of N=C(NMe_2)P(NMe_2)$_2$ group were not described in the literature, it was difficult to estimate the rate of the cyclization and whether it would be stable or not.

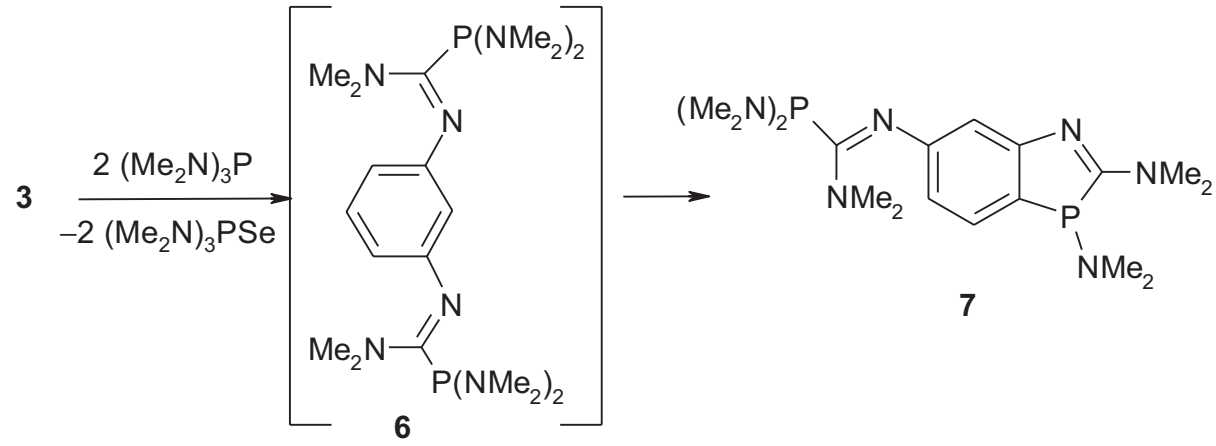
The reaction of compound **3** with two equivalents of hexamethylphosphorus triamide was monitored by ^{31}P NMR spectroscopy at room temperature. ^{31}P NMR spectra indicated a gradual disappearance of hexamethylphosphorus triamide (δ_p 123 ppm) and the appearance of tris(dimethylamino) phosphane selenide (δ_p 84 ppm) and compound **7** (δ_p 95 and 59 ppm) (Scheme 3). In a month, the reaction came to completion. The solvents were carefully evaporated keeping temperature below 20°C.

We have isolated compound **7** in a mixture with tris(dimethylamino)-phosphane selenide. It was characterized by ^{31}P, ^{1}H, and ^{13}C NMR spectroscopy. In ^{13}C NMR spectrum, compound **7** showed resonance typical for the formamidine carbon at 161.8 (d, J = 30 Hz) ppm and for the benzazaphosphole carbon at 176.5 (d, J = 23 Hz) ppm. Heating this mixture led to compounds **8** and **9** (Scheme 4). Compound **6** was not registered by ^{31}P NMR spectroscopy. Therefore, one can draw a conclusion that electron-donating capability of the —N=C(NMe_2)P(NMe_2)$_2$ group is equal or greater of that of NMe_2.

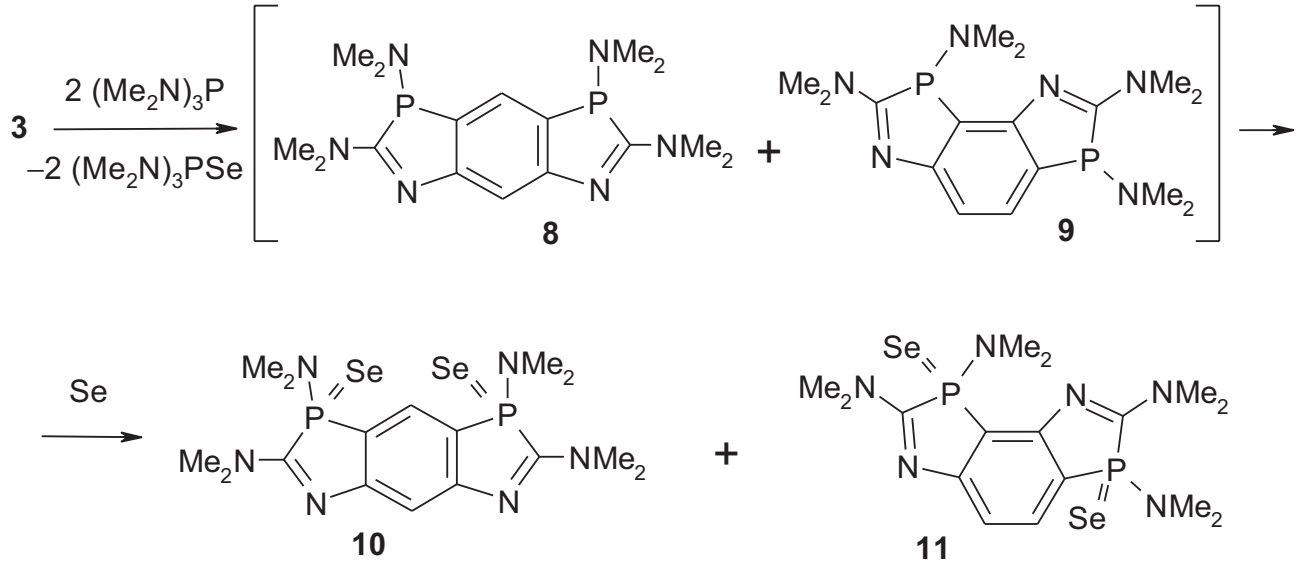
Thus, the reduction of compound **3** easily proceeds at room temperature, but slight heating is sufficient to complete the second cyclization step (Scheme 4). The intermediate **7** has two possibilities for the cyclization: into linear **8** or angular **9**. As trivalent phosphorus derivatives are labile compounds, they were oxidized into penatavalent derivatives **10** and **11** and separated by chromatography as mixtures of diastereomers. The first fraction (R_f 0.03–0.15) was compound **10**, and two other fractions (R_f 0.3–0.4 and 0.5–0.7) were proved to be



SCHEME 1 Synthesis of P(V) formamidine **3**.



SCHEME 3 Preparation of the intermediate compound **7**.



SCHEME 4 Synthesis of compounds **10** and **11**.

compound **11**. Both in ^{1}H and ^{13}C spectra, characteristic features of compound **10** are triplets coupled to phosphorus atoms. Compound **11** lacks such symmetry (Fig. 2).

As we failed to grow a single crystal of compound **10**, it was reduced to trivalent derivative **6** and converted into sulfur analog **12**, which was studied by the single crystal X-Ray analysis (Scheme 5).

The perspective view of **12** is given in Fig. 3. The central tricyclic system C(1–8)P(1)P(2)N(1)N(2) is almost planar (the maximum deviation from the least-square plane is 0.050 Å). The terminal N(3), N(4), and N(5) atoms have a trigonal-planar bond configuration (corresponding sum of the bond angles is 359.9(9)^3, 360.0(1)^3, and 357.0(9)^3), and the N(6) atom has a pyramidal bond configuration (sum of the bond angles is 352.2(9)^3).

Furthermore, we have investigated the analogous transformation of 1,3,5-triaminobenzene. We have started with the synthesis of compound **14** that was prepared by reacting 1,3,5-triaminobenzene with *N*,*N*-dimethyl-*P*-(trichloromethyl) phosphonamidous chloride (Scheme 6). Compound **14** was characterized by ^{31}P NMR and further transformed into selenide **15** possessing three chiral phosphorus atoms. Compound **15** as the mixture of diastereomers was treated with an excess of dimethylamine to give a high melting compound **16**. Pentavalent *C*-phosphorylated formamidine **16** was reduced with hexamethylphosphorus triamide in 5 min at room temperature, but the intermediate trivalent *C*-phosphorylated amidine was not registered as it immediately cyclized into azaphosphole **17**. The latter was readily oxidized to pentavalent

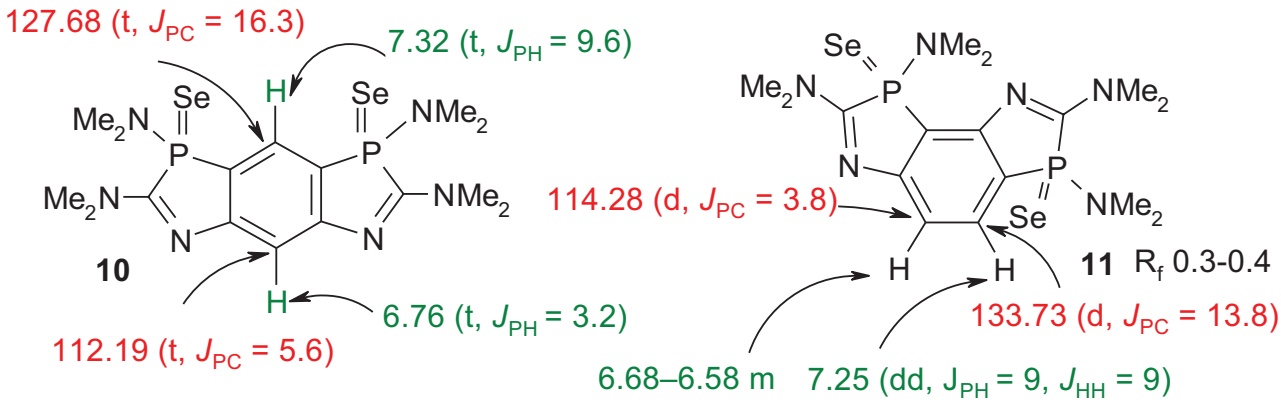
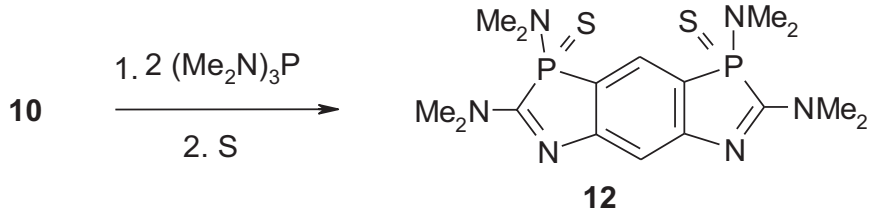


FIGURE 2 Characteristic NMR data for compounds **10** and **11**.



SCHEME 5 Synthesis of compound **12**.

derivatives **18a–c**. The molecular structure of **18b** was confirmed by single-crystal X-ray diffraction (Fig. 4).

The perspective view of the molecule **18b** is given in the Fig. 4. The molecule of **18b** has three chiral tetrahedral phosphorus atoms and crystallizes in a chiral space group ($P2_12_12_1$). The five-membered heterocycles, which are adjacent to the central C(1–6) cycle, are not planar and have an *envelope* conformation: atoms C(5)C(4)N(4)C(9) are planar within 0.002 Å, and the "corner" C(5)P(3)C(9) forms with this plane the dihedral angle of 4.61°; the dihedral angle between C(3)C(2)N(1)C(8) (planar within 0.003 Å) and C(3)P(2)C(8) is 8.61°; the dihedral angle between C(1)C(6)N(7)C(7) (planar within 0.015 Å) and C(1)P(1)C(7) is 3.36°. The N(2), N(5), N(6), and N(8) atoms have a trigonal-planar bond configuration (corresponding sum of the bond angles is 360.0°, 359.9°, 357.5°, and 360.0°), and the N(3) and N(9) atoms have a pyramidal bond configuration (sum of the bond angles is 352.8° and 349.9°, correspondingly).

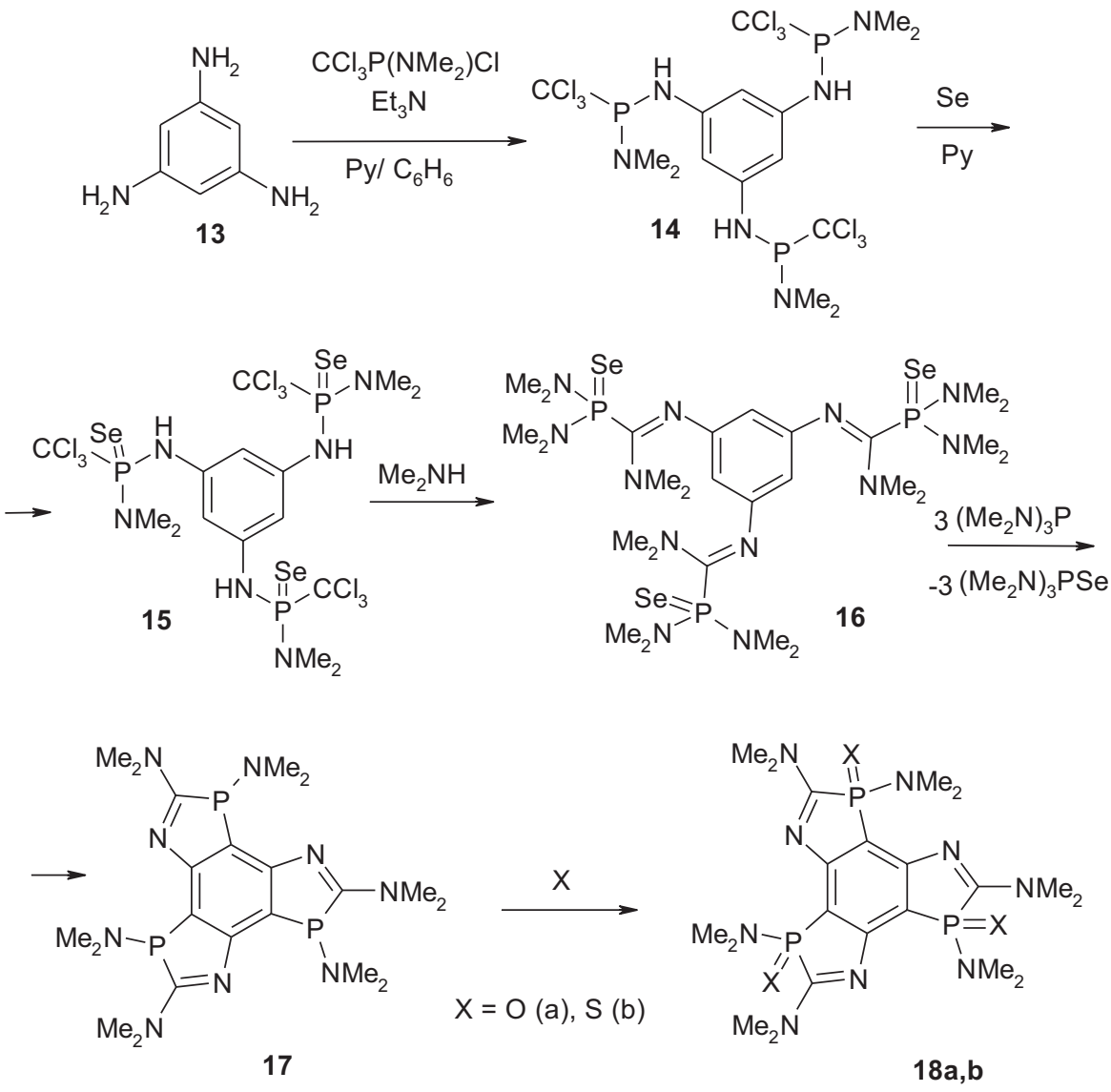
CONCLUSIONS

C-phosphanyl(*N*-aryl)formamidines derived from 1,3-diaminobenzene and 1,3,5-triaminobenzene undergo intramolecular cyclocondensations furnishing tricyclic and tetracyclic azaphospholes, respectively. Interestingly, the double and the triple intramolecular cyclocondensations proceed more efficiently than formerly reported reaction involving monoaminobenzene derivatives [6]. Therefore, a facile synthetic route to 1,3-azaphospholes starting from 1,3-diaminobenzene and 1,3,5-triaminobenzene was developed.

EXPERIMENTAL

General

All procedures with air and moisture sensitive compounds were performed under an atmosphere of dry argon in flame-dried glassware. Solvents were purified and dried by standard methods. Melting points (mp) were determined with an electrothermal capillary melting point apparatus and were uncorrected. ^{1}H spectra were recorded on a Bruker Avance DRX 500 (500.13 MHz) or Varian VXR-300 (299.94 MHz) spectrometer. ^{13}C NMR spectra were recorded on a Bruker Avance DRX 500 (125.75 MHz) spectrometer. ^{31}P NMR spectra were recorded on a Varian VXR-300 (121.42 MHz) spectrometer. Chemical shifts (δ) are reported in ppm downfield relative to internal tetramethylsilane (TMS) (for ^{1}H and ^{13}C spectra) and external 85% H_3PO_4 (for ^{31}P spectra). Chromatography was performed on silica gel Gerudan SI60. Elemental analyses were performed at the microanalytical laboratory of the Institute of the



SCHEME 6 Synthesis of compound **18**.

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EXPERIMENTAL

All crystallographic measurements were performed at 173 K on a Bruker Smart Apex II diffractometer (Mo$K\alpha$). Data were corrected for Lorentz and polarization effects. The SADABS procedure [7] absorption correction was applied. The structures were solved by direct methods and refined by the full-matrix least-squares technique in the anisotropic approximation using the SHELXS97 and SHELXL97 programs [8, 9] and CRYSTALS program package [10]. In the refinement, the Chebychev weighting scheme [11] was used. All hydrogen atoms were located in the difference Fourier maps and refined with fixed positional and thermal parameters. The absolute configuration was determined by the Flack method [12]. Enantiopole parameters are 0.01(1) (2557 Friedel pairs) for **18b** and 0.04(7) (1989 Friedel pairs) for **12**.

Full crystallographic details have been deposited at Cambridge Crystallographic Data Centre (CCDC) (Table 1).

N′,N″-1,3-Phenylenebis[1,1-bis(dimethylamino)-N,N-dimethylphosphinecarboximidamide] Diselenide **2**. 1,3-diaminobenzene (760 mg, 7 mmol) and triethylamine (2.7 mL) in pyridine (20 mL) were added to *N*,*N*-dimethyl-*P*-(trichloromethyl) phosphonamidous chloride (3.2 g, 14 mmol) at

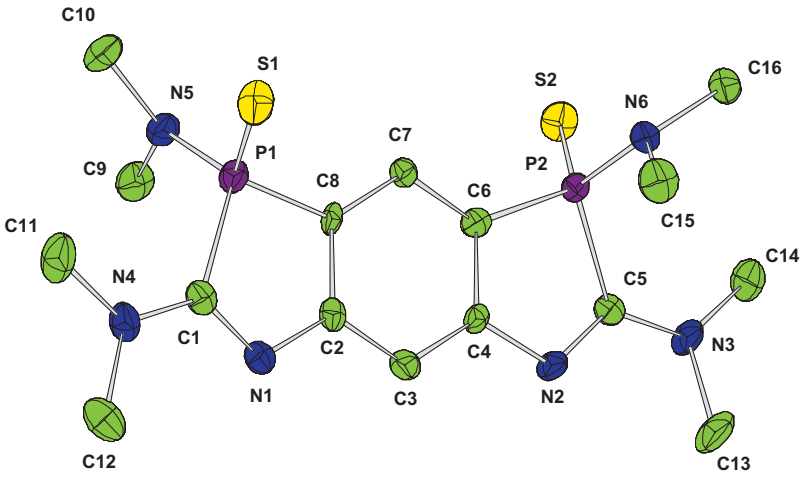

FIGURE 3 X-ray molecular structure for **12**. Selected bond lengths [Å] and angles [°]: S(1)-P(1) 1.940(1), S(2)-P(2) 1.947(1), P(1)-N(5) 1.652(3), P(1)-C(1) 1.871(4), P(1)-C(8) 1.793(4), P(2)-N(6) 1.664(3), P(2)-C(5) 1.872(4), P(2)-C(6) 1.781(4); C(1)P(1)C(8) 87.5(2), C(5)P(2)C(6) 88.9(2), C(1)N(1)C(2) 110.5(3), and C(4)N(2)C(5) 111.4(3).

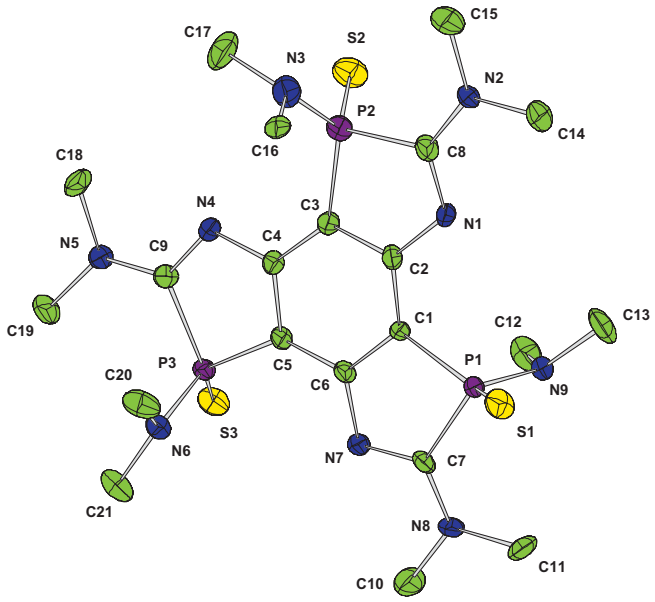

FIGURE 4 Molecular structure for **18b**.

–10°C. The reaction mixture was stirred at room temperature for 15 h. Selenium (1.5 g, 19 mmol) was added, and the reaction mixture was stirred at 25°C for 30 h. The pyridine was evaporated under reduced pressure. Acetonitrile (25 mL) was added to the residue, the solution was refined with charcoal, which was then filtered off, and the filtrate evaporated. The residue was extracted with boiling diethyl ether (2 × 50 mL). The ether was evaporated to 10 mL, cooled to –6°C, and the precipitated solid was collected by filtration to give off mixture of isomers (3.19 g, 70%). The isomers were separated using silica gel chromatography. R_f 0.15–0.20 (eluent—ethyl acetate: hexane 1:5), (1.02 g, 32%), mp 97–100°C. ^{31}P ($CDCl_3$): δ 70.3. ^{1}H ($CDCl_3$, 300 MHz): δ 7.24 (t, 1H, J 7.8 Hz, H_{Ar}), 6.97 (m, 1H, H_{Ar}), 6.81 (dd, 2H, J_1 2.1 Hz, J_2 8.1 Hz, H_{Ar}), 5.21 (d, 2H, J 11.4 Hz, NH), 3.09 (d, 12H, J 10.8 Hz, NCH_3). ^{13}C ($CDCl_3$): δ 139.7, 130.3, 114.85 (d, J 6 Hz), 111.2 (t, J 4 Hz), 98.8 (d, J 65 Hz, CCl_3), 39.9 (d, J 4 Hz).

R_f 0.4–0.45 (ethylacetate: hexane 1:5); (1.45 g, 45%), mp 176–178°C. ^{1}H ($CDCl_3$, 500 MHz): δ 7.27 (m, 1H, H_{Ar}), 7.19 (t, 1H, J 8.0 Hz, H_{Ar}), 6.57 (dd, 2H, J_1 2.0 Hz, J_2 8.0 Hz, H_{Ar}), 5.14 (d, 2H, J 5.75 Hz, NH), 3.17 (d, 12H, J 11.0 Hz, NCH_3). ^{13}C ($CDCl_3$): δ 139.6, 130.3, 113.5 (d, J 10.0 Hz), 107.0 (m), 98.5 (d, J 65 Hz, CCl_3), 39.8 (d, J 5 Hz). ^{31}P ($CDCl_3$): δ 68.8.

N′,N″-1,3-Phenylenebis[1,1-bis(dimethylamino)-N,N-dimethyl-phosphine-carboximidamide] Diselenide **3**. A 10-mL vial was charged with a mixture of isomers **2** (1.0 g, 1.5 mmol) and dimethylamine (5 mL). The vial was sealed and the solution was stirred at 25°C for 24 h. An excess dimethylamine was removed; the solid residue was washed with degassed water (2 × 3 mL). The solid was dried and recrystallized from diethyl ether (14 mL) and left at –6°C. The precipitated crystals were collected and dried to give the target crystalline product **3** (860 mg, 91%); mp 156–157°C.

^{1}H (DMSO-d_6, 300 MHz): δ 7.04 (t, 1H, J 8.1 Hz, CH_{Ar}), 6.30 (dd, 2H, J_1 2.4 Hz, J_2 7.8 Hz, CH_{Ar}), 6.20 (m, 1H, CH_{Ar}), 2.89 (s, 12H, CH_3), 2.78 (d, 24H, J 12 Hz, CH_3).

^{13}C (DMSO-d_6, 125.8 MHz): δ 151.4 (d, J 148 Hz, CN), 150.3 (d, J 20 Hz, C-1,3), 128.1 (C-2), 113.6 (C-6,4), 112.4 (C-5), 41.2 (d, J 1.25 Hz), 38.1. ^{31}P

TABLE 1 The Main Crystallographic Parameters of the Compounds **18b** and **12**

Compound	**18b**	**12**
Cell parameters		
a [Å]	10.9963(5)	23.8355(8)
b [Å]	12.5231(6)	8.0813(3)
c [Å]	21.6119(9)	10.9865(4)
α [°]	90	90
β [°]	90	90
γ [°]	90	90
V [Å^3]	2976.1(2)	2116.24(13)
Z	4	4
D [g·cm^{-3}]	1.347	1.345
Crystal system	Orthorhombic	Orthorhombic
Space group	$P2_12_12_1$	$Pna2_1$
μ [cm^{-1}]	0.439	0.416
F(000)	1272	904
Indices	$10 \geq h \geq -13$	$24 \geq h \geq -30$
	$14 \geq k \geq -15$	$10 \geq k \geq -10$
	$26 \geq l \geq -16$	$13 \geq l \geq -13$
θ_{max} [°]	26.59	26.68
Number of reflections:		
collected	15643	16689
independent	5917	4328
in refinement ($I \geq 3\sigma(I)$)	4616	3252
R(int)	0.045	0.061
Number of refined parameters	325	235
Observed/Variable	14.2	13.8
Final *R* indices		
R_1 (F)	0.0532	0.0427
R_w (F)	0.0579	0.0416
GOF	1.1139	1.1088
Weighting coefficients	1.33	1.40
	− 0.389	− 1.27
	0.772	1.13
	− 0.122	− 0.439
		0.203
Largest peak/hole [e·cm^{-3}]	0.78/−0.64	0.37/−0.30
CCDC deposition number	933777	933776

($CDCl_3$): δ 67.5. MS (EI, 70eV): *m/z* (%) = 612.8 (98.95) $[M]^+$.

N′-[2,3-Bis(dimethylamino)-3H-1,3-benzazaphosphol-6-yl]-1,1-bis(dimethylamino)-N,N-dimethylphosphinecarboximidamide **7** *(The Mixture with Tris(dimethylamino)-phosphane Selenide).* Hexamethylphosphorus triamide (990 mg, 6.1 mmol) was added to a solution of compound **3** (1.28 g, 2.1 mmol) in benzene (5 mL). The reaction mixture was kept for 1 month at room temperature. The solvent was evaporated under reduced pressure and then was kept in vacuo 0.05 Torr maintaining temperature below 20°C. The residue was analyzed by NMR spectroscopy.

^{31}P (C_6D_6): δ 59, 95, 84. ^{1}H (C_6D_6, 500 MHz): δ 7.40–7.36 (m, 1H, H_{Ar}), 7.16 (s, 1H, H_{Ar}), 6.6–6.4 (m, 1H, H_{Ar}), 2.71 (s, 6H, NCH_3), 2.48 (d, 12H, J_{PH} 9Hz, NCH_3), 2.4–2.5 (m, 52H, $PNMe_2$, NMe_2 + $SeP(NMe_2)_3$); ^{13}C NMR (125 MHz, C_6D_6) δ 176.46 (d, $J = 23$ Hz), 161.84 (d, $J = 30$ Hz), 160.31 (d, $J = 9$ Hz), 154.96 (d, $J = 3.8$ Hz), 128.70, 128.49, 127.88, 127.69, 127.50, 118.60 (d, $J = 11.3$ Hz), 114.19, 114.18, 114.14, 114.12, 111.84 (d, $J = 2.5$ Hz), 111.43, 41.47, 41.46, 41.34, 41.33, 41.25, 41.15, 39.24 (d, $J = 9$ Hz), 37.49 (d, $(Me_2N)_3PSe$ $J = 3.8$ Hz).

N,N,N′,N′,N″,N″,N‴,N‴-Octamethyl-3,5-diselenoxo-3,5-dihydro-1,7-diaza-3λ^5,5λ^5-diphospha-s-indacene-2,3,5,6-tetraamine **10** *and N^2,N^2,N^3,N^3,N^7,N^7,N^8,N^8-Octamethyl-3,8-diselenoxo-3,8-dihydro-1,6-diaza-3λ^5,8λ^5-diphospha-as-indacene-2,3,7,8-tetraamine* **11**. Hexamethylphosphorus triamide (990 mg, 6.1 mmol) was added to a solution of compound **3** (1.28 g, 2.1 mmol) in benzene (5 mL). The reaction mixture was kept for 20 h at room temperature. The solvent was evaporated and then the excess hexamethylphosphorus triamide was distilled off in vacuo 0.05 Torr/100°C. The residual oil (1.5 g) exhibiting two main signals of P(III) compounds **8** and **9** in ^{31}P NMR spectrum—57.52 and 56.14 as well as signal of tris(dimethylamino)phosphane selenide 83.2 was dissolved in benzene (14 mL) and finely ground selenium (500 mg, 6.3 mmol) was added. The reaction mixture was stirred for 2 h at 60°C. Excess selenium was filtered off; the solvent was evaporated to give solid residue (1.11 g). The solid was separated by silica gel chromatography using ethylacetate as eluent.

Compound 10 R_f 0.03–0.15; (0.72g, 66%), mp 258–260°C. ^{31}P ($CDCl_3$): δ 53.02 (d, J_{PSe} = 795 Hz), 52.85 (d, J_{PSe} = 785 Hz). ^{1}H ($CDCl_3$, 400 MHz): δ 7.28 (t, 1H, J_{HH} 9.6 Hz, H_{Ar}), 6.76 (t, 1H, J_{HH} 3.2 Hz, H_{Ar}), 3.38 (s, 6H, NCH_3), 3.24 (s, 6H, NCH_3), 2.74 (d, 12H, J_{PH} 12 Hz, NCH_3).

^{13}C NMR (125 MHz, $CDCl_3$) δ 166.30 (d, $J = 69$ Hz), 161.42 (d, $J = 2.5$ Hz), 161.16 (d, $J = 2.5$ Hz), 127.68 (t, $J = 16.3$ Hz), 115.7 (d, $J = 13.8$ Hz), 114.76 (d, $J = 13.8$ Hz), 112.19 (t, $J = 5.6$ Hz), 39.03, 38.94, 38.93, 38.92, 36.76, 36.75, 36.73.

MS (EI, 70eV): *m/z* (%) = 523.0, 527.0, 528.9. Anal. calcd for $C_{16}H_{26}N_6P_2Se_2$ C 36.80, H 5.02, N 16.09, P 11.86. Found: C 36.32, H 4.61, N 16.41, P 12.05.

Compound 11 R_f 0.3–0.4; (50 mg, 4%), mp 224–226°C. ^{31}P ($CDCl_3$): δ 54.33 (d, J_{PSe} = 804 Hz), 54.30 (d, J_{PSe} = 804 Hz), 51.62 (d, J_{PSe} = 793 Hz), 51.59 (d, J_{PSe} = 793 Hz). ^{1}H ($CDCl_3$, 400 MHz): δ 7.25 (dd, 1H, J_{HH}, 8 J_{PH} 10 Hz, H_{Ar}), 6.68–6.58 (m, 1H, H_{Ar}), 3.42 (s, 3H, NCH_3), 3.34 (s, 3H, NCH_3), 3.21 (s, 6H,

NCH_3), 2.73 (d, 6H, J_{PH} 8 Hz, NCH_3), 2.70 (d, 6H, J_{PH} 8 Hz, NCH_3). ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.37 (d, $J = 21.4$ Hz), 165.78 (d, $J = 30.2$ Hz), 160.32 (d, $J =$ 2.5 Hz), 160.10 (d, $J = 2.5$ Hz), 156.51 (d, $J = 8.8$ Hz), 156.25 (d, $J = 8.8$ Hz), 133.73 (d, $J = 13.8$ Hz), 115.48 (d, $J = 7.5$ Hz), 114.51 (d, $J = 7.5$ Hz), 114.37 (d, $J = 5$ Hz), 114.28 (d, $J = 3.8$ Hz), 109.74 (d, $J =$ 6.3 Hz), 108.88 (d, $J = 7.5$ Hz), 39.35, 38.97 (d, $J =$ 2.5 Hz), 38.79, 38.75, 37.05 (d, $J = 3.7$ Hz), 36.62 (d, $J = 3.7$ Hz), MS (EI, 70eV): *m/z* (%) = 522.0, 523.0, 529.0.

R_f 0.5–0.7; (96 mg, 9%), mp 269–270°C. ^{31}P ($CDCl_3$): δ 54.20 (d, $J_{PSe} = 792$ Hz), 54.17 (d, $J_{PSe} =$ 792 Hz), 51.38 (d, $J_{PSe} = 782$ Hz), 51.34 (d, $J_{PSe} =$ 782 Hz).

^1H ($CDCl_3$, 500 MHz): δ 7.28 (dd, 1H, J_{HH}, 9 J_{PH} 9 Hz, H_{Ar}), 6.74–6.64 (m, 1H, H_{Ar}), 3.45 (s, 3H, NCH_3), 3.37 (s, 3H, NCH_3), 3.25 (s, 3H, NCH_3), 3.24 (s, 3H, NCH_3), 2.77 (d, 12H, J_{PH} 13 Hz, NCH_3). ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.72, 166.18, 165.55, 160.38 (d, $J = 2.5$ Hz), 160.15 (d, $J = 2.5$ Hz), 156.27 (d, $J = 8.8$ Hz), 156.01 (d, $J = 10.1$Hz), 133.70 (d, $J = 16.3$ Hz), 115.38 (d, $J = 7.5$ Hz), 114.53 (d, $J =$ 3.7 Hz), 114.45, 114.43, 114.41, 114.37 m, 110.37 (d, $J = 6.3$ Hz), 109.53 (d, $J = 6.3$ Hz), 39.35 m, 38.99 (d, $J = 2.5$ Hz), 38.73 (d, $J = 3.8$ Hz), 38.63 m, 37.03 (d, J = 3.8 Hz), 36.90 (d, $J = 5$ Hz), MS (EI, 70eV): *m/z* (%) = 522.9, 527.0, 528.9. Anal. calcd for $C_{16}H_{26}N_6P_2Se_2$ C 36.80, H 5.02, N 16.09, P 11.86. Found: C 36.41, H 4.73, N 16.44, P 11.98.

N, N, N′, N′, N″, N″,N‴,N‴-Octamethyl-3,5-dithioxo-3,5-dihydro-1, 7-diaza-3λ^5,5λ^5-diphospha-s-indacene-2,3,5,6-tetraamine **12**. Hexamethylphosphorus triamide (410 mg, 2.5 mmol) was added to a solution of compound **10** (522 mg, 1 mmol) in benzene (10 mL). In 5 min, all volatiles were evaporated in vacuo 0.05 Torr/150°C. The residue was dissolved in benzene (10 mL) and finely ground sulfur (65 mg, 2 mmol) was added. The reaction mixture was heated at 40°C with stirring till complete dissolution of the sulfur. The solvent was evaporated under reduced pressure. The residue was recrystallized from acetonitrile (1.5 mL) to give the target product **12** as yellow solid (120 mg, 28%), mp 310°C (decomp.). ^{31}P (DMSO-d_6): δ 61.6. ^1H (DMSO-d_6, 300 MHz): δ 7.12–7.18 (m, 1H, H_{Ar}), 6.55 (t, 1H, J 3.6 Hz, H_{Ar}), 3.31 (s, 6H, P-NCH_3), 3.16 (s, 6H, P-NCH_3), 2.64 (d, 12H, J 12.3 Hz, NCH_3). ^{13}C (DMSO-d_6): δ 166.8 (d, J 78 Hz, C = N), 161.25 (d, J 4 Hz, 1,5-C_{Ar}), 161.0 (d, J 2.5 Hz, 1,5-C_{Ar}), 126.3–126.7 (m, 3-C_{Ar}), 114.3 (d, J 12.6 Hz, 2,4-C_{Ar}), 113.2 (d, J 13.8 Hz, 2,4-C_{Ar}), 110.7 (br s, 6-C_{Ar}), 38.2 (d, J 24 Hz, $PNCH_3$), 35.11 (s, NCH_3). MS (EI, 70eV): *m/z* (%) = 429.0 (92.5) $[M-H]^+$. Anal. calcd for $C_{16}H_{26}N_6P_2S_2$ C 44.85, H 6.12, N 19.61, P 14.46. Found: C 44.45, H 6.29, N 19.38, P 14.12.

N′,N‴,N⁗-Benzene-1,3,5-triyltris[N,N-dimethyl-P-(trichloromethyl) (phosphonous diamide)] **14**. A solution of benzene-1,3,5-triamine **13** (670 mg, 5.4 mmol) and triethylamine (1.9 g, 18.8 mmol) in pyridine (10 mL) was added to a solution of *N*, *N*-dimethyl-*P*-(trichloromethyl) phosphonamidous chloride (4.12 g, 17.9 mmol) in benzene (4mL). The reaction mixture was stirred at 15°C for 15 h. The solvent was evaporated under reduced pressure at 30°C and to the residue, Et_2O (70 mL) was added. The insoluble residue was filtered off and the mother liquor was evaporated under reduced pressure. Then the product was extracted with pentane (2 × 50 mL), the extract was evaporated under reduced pressure to dryness and used in the next step without further purification. Yield: 2.41g (63.7%); mp: 35–40°C. ^{31}P NMR (Et_2O), δ: 73.

N′,N‴,N⁗-Benzene-1,3,5-triyltris[N,N-dimethyl-P-(trichloromethyl)(phosphonosele-noic diamide)] **15**. To a stirred solution of **14** (2.4 g, 3.4 mmol) in pyridine (10 mL), selenium (1.5 g, 10 mmol) was added in one portion and the reaction mixture was left at 15°C for 72 h. The solvent was evaporated under reduced pressure and the residue was washed with H_2O (20 mL) and MeOH (10mL), successively. Then the isoluble residue was additionally washed on filter with MeOH (5 × 10 mL) and dried to give **15** (1.97 g). The mother liquor was evaporated under reduced pressure and the resulting residue was triturated with H_2O (10 mL) and MeOH (10 mL) giving white solid **15** (0.25 g), combined yield 69%, mp 140°C (dec). ^{31}P NMR (pyridine), δ: 71.5. ^1H ($CDCl_3$, 300 MHz), a mixture of three diastereomers in a ratio of 1/0.9/2, δ: 7.02 (s, 1H, CH_{Ar}), 6.61 (s, 1H, CH_{Ar}), 6.41 (s, 1H, CH_{Ar}), 5.166 (d, 3H, J 11.7 Hz, 3NH), 3.18 (d, 6H, J 10.8 Hz, NCH_3), 3.16 (d, 6H, J 10.8 Hz, NCH_3), 3.10 (d, 6H, J 10.8 Hz, NCH_3). Anal. calcd for $C_{15}H_{24}Cl_9N_6P_3Se_3$ N 8.97, P 9.91. Found: N 9.32, P 10.21.

N′,N″,N‴-Benzene-1,3,5-triyltris[1,1-bis(dimethylamino)-N, N-dimethylphosphinecar-boximidamide] triselenide **16**. A mixture of selenide **15** (1.9 g, 2 mmol) and condensed dimethylamine (9 mL) was stirred for 20 h at 15°C in a pressure tube. Then the tube was opened allowing the dimethylamine evaporating. The residue was washed with H_2O and dried under reduced pressure. The residue was dissolved in benzene and treated with charcoal, filtered, and evaporated under reduced pressure. The residue was washed with hexane and recrystallized

from CH_3CN (16 mL) to give **16** 1.15g (65%). Mp 187–189°C. ^{31}P NMR (Et_2O), δ: 65.1. ^1H ($CDCl_3$, 500 MHz), δ: 5.71 (s, 3H, CH_{Ar}), 2.87 (s, 18H, NCH_3), 2.30 (d, 36H, J 11.0 Hz, NCH_3). ^{13}C ($CDCl_3$): δ 151.05 (d, J 147 Hz, CN), 150.2 (d, J 20 Hz, i-C_{Ar}), 105.7, 41.1 (d, J 2.5 Hz), 38.1 (d, J 1.3 Hz). Anal. calcd for $C_{27}H_{57}N_{12}P_3Se_3$ N 19.11, P 10.56. Found: N 19.45, P 10.73.

N, N, N′, N′, N″, N″, N‴, N‴, N⁗, N⁗, N⁗′, N⁗′-Dodecamethyl-1,4,7-triaza-3,6,9-triphosphatrindene-2,3,5,6,8hexaamine **17**. To a stirred solution of amidine **16** (2.93 g, 3.3 mmol) in benzene (15 mL), hexamethylphosphorus triamide (1.96 g, 12 mmol) was added in one portion and the reaction mixture was left at 15°C for 5 min. Then, the volatiles were removed under reduced pressure and tris(dimethylamino)phosphane selenide was distilled off in vacuo (bp 120–130°C/ 0.05 mmHg). The residue was placed in a pressure tube and the product was extracted with pentane at 100°C (80 mL). The resulting solution was concentrated to 50 mL and cooled to 17°C to give an orange precipitate. The precipitate was filtered and dried under reduced pressure to give yellow solid **17** (1.0 g, 59%). ^{31}P (C_6D_6, 202 MHz): δ 61.7, 61.4, 61.3. ^1H (C_6D_6, 300 MHz): δ 2.63, 2.67, 2.70 td, 2.61–2.72 m (18H, J 10.2 Hz, NCH_3), 2.89 (9H, m, NCH_3), 2.99 (br s, 9H, NCH_3).

N, N, N′, N′, N″, N″, N‴, N‴, N⁗, N⁗, N⁗′, N⁗′-Dodecamethyl-3,6,9-trioxo-6,9-dihydro-3H-1,4,7-triaza-3λ⁵,6λ⁵,9λ⁵-triphospha-trindene-2,3,5,6,8 hexaamine **18a**. To a stirred solution of **17** (100 mg, 0.2 mmol) in CH_2Cl_2 (2 mL), H_2O_2 (0.1 mL, 30% aqueous) was added in one portion and the reaction mixture was left at 17°C for 10 min. The solvent was evaporated under reduced pressure and the residue was recrystallized from Et_2O (5 mL) to give yellow solid (21 mg, 20%). Mp 212–213°C.

^{31}P ($CDCl_3$): δ 32.7 (88.5%); 18.8 (11.5%). ^1H ($CDCl_3$, 300 MHz): δ 2.62–2.72 (m, 18H, NCH_3), 3.20 (m, 9H, C-NCH_3), 3.34 (m, 9H, C-NCH_3).

N, N, N′, N′, N″, N″, N‴, N‴, N⁗, N⁗, N⁗′, N⁗′-Dodecamethyl-3,6,9-trithioxo-6,9-dihydro-3H-1,4,7-triaza-3λ⁵,6λ⁵,9λ⁵-triphospha-trindene-2,3,5,6,8hexaamine **18b**. To a stirred solution of **17** (520 mg, 1.02 mmol) in benzene (6 mL), finely powdered elemental sulfur (100 mg, 3.11 mmol) was added in one portion and the reaction mixture was left at 70°C for 1 h. After cooling to ambient temperature, benzene (45 mL) was added to the reaction mixture and insoluble components were separated by filtration. The mother liquor was evaporated under reduced pressure and the residue was recrystallized from CH_3CN (25 mL) to give yellow solid (414 mg, 67%). Mp 330–332°C. ^{31}P ($CDCl_3$): δ 59.7. ^1H ($CDCl_3$, 300 MHz): δ 2.73 (dd, 18H, J_1 9.0 Hz, J_2 13.0 Hz, NCH_3), 3.23+3.24 (s, 9H, C-NCH_3), 3.41+3.42 (s, 9H, C-NCH_3).

Anal calcd. for $C_{21}H_{36}N_9P_3S_3$ N 20.88, P 15.39. Found: N 21.09, P 15.54.

REFERENCES

[1] (a) Bansal, R. K.; Heinicke, J Chem Rev 2001, 101, 3549; (b) Bansal, R. K.; Gupta, N.; Kumawat, S. K. Curr Org Chem 2007, 11, 33; (c) Bansal, R. K. Top. Heterocycl. Chem. 2009, 20, 1.

[2] (a) Heinicke, J.; Gupta, N.; Surana, A.; Peulecke, N.; Witt, B.; Steinhauser, K.; Bansal, R. K.; Jones, P. G. Tetrahedron 2001, 57, 9963; (b) Heinicke, J.; Surana, A.; Peulecke, N.; Bansal, R. K.; Murso, A.; Stalke, D. Eur J Inorg Chem 2001, 2563; (c) Surana, A.; Singh, S.; Bansal, R. K.; Peulecke, N.; Spannenberg, A.; Heinicke, J.; J Organomet Chem 2002, 646, 113; (d) Heinicke, J.; Steinhauser, K.; Peulecke, N.; Spannenberg, A.; Mayer, P.; Karaghiosoff, K. Organometallics 2002, 21, 912; (e) Heinicke, J.; Gupta, N.; Singh, S.; Surana, A.; Kühl, O.; Bansal, R. K.; Karaghiosoff, K.; Vogt, M. Z Anorg Allg Chem 2002, 628, 2869; (f) Doherty, S.; Knight, J. G.; Scanlan, T. H.; Elsegood, M. R. J.; Clegg, W. J Organomet. Chem 2002, 650, 231; (g) Adam, M. S. S.; Jones, P. G.; Heinicke, J. W. Eur J Inorg Chem 2010, 3307; (h) Aluri, B. R.; Niaz, B.; Kindermann, M. K.; Jones, P. G.; Heinicke, J. Dalton Trans 2011, 40, 211.

[3] Zhang, J.-P.; Zhang, Y.-B.; Lin, J.-B.; Chen, X.-M. Chem Rev 2012, 112, 1001.

[4] Choi, H.-J.; Park, Y. S.; Yun, S. H.; Kim, H.-S.; Cho, C. S.; Ko, K.; Ahn K. H. Org Lett 2002, 4(5), 795.

[5] Wilkens, H.; Ostrowski, A.; Jeske, J.; Ruthe, F.; Jones, P. G.; Streubel, R. Organometallics 1999, 18, 5627.

[6] (a) Marchenko, A.; Koidan, G.; Hurieva, H.; Merkulov, A.; Pinchuk, A. Y.; Kostyuk, A. Tetrahedron 2010, 66, 3668; (b) Marchenko, A.; Koidan, H.; Hurieva, H.; Merkulov, A.; Pinchuk, A. Y.; Rozhenko, A. B.; Jones, P. G.; Thönnesen, H.; Kostyuk, A. Tetrahedron 2011, 67, 7748.

[7] Sheldrick, G. M. SADABS: Program for scaling and correction of area detector data; University of Göttingen: Göttingen, Germany, 1996.

[8] Sheldric, G. M. SHELXS97. Program for the solution of crystal structure; University of Göttingen: Göttingen, Germany, 1997.

[9] Sheldric, G. M. SHELXL97. Program for the refinement of crystal structures; University of Göttingen: Göttingen, Germany, 1997.

[10] Watkin, D. J.; Prout, C. K.; Carruthers, J. R.; Betteridge, P. W. CRYSTALS Issue 10. Oxford: Chemical Crystallography Laboratory, University of Oxford, 1996.

[11] Carruthers, J. R.; Watkin, D. J. Acta Crystallogr, Sect C: Cryst Struct Commun 1979, 35, 698.

[12] Flack, H. D. Acta Crystallogr 1983, A39, 876.