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Reaction of *N*-Thioamido Amidines with Phosphoramide Derivatives: Synthesis of 2-Substituted-1,3,5,2-Triazaphosphorines

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ABSTRACT: *The reaction of N-thioamido amidines* **1** *with tris(dimethylamino)phosphine or bis(diethylamino)phenylphosphine in refluxing toluene leads to the 1,3,5,2λ³-triazaphosphorines* **2** *and* **3**, *respectively. The condensation results in the release of two molecules of dialkylamine. The sulfuration of the trivalent phosphorus atoms was achieved by the reaction with elemental sulfur, followed by heating in toluene. The structure of the triazaphosphorines* **2** *and* **3** *and their thione derivatives* **4** *and* **5** *were readily elucidated by means of* ^{1}H, ^{13}C, *and* ^{31}P *NMR spectroscopy and mass spectrometry*. © 2009 Wiley Periodicals, Inc. Heteroatom Chem 20:272–277, 2009; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.20546

INTRODUCTION

Among the five- and six-membered heterocycles containing carbon, nitrogen, and phosphorus atoms and in particular those containing more than two heteroatoms such as diazaphosphole, triazaphosphole, diazaphosphorine, and triazaphosphorine rings, the latter are the least studied [1–10]. Since 1966 when Latscha isolated triazaphosphorines as byproducts of the reaction of phosphorus pentachloride with dimethylurea [11], much work was devoted to the development of new routes to these heterocycles [12–14]. Recently Schmutzler and his coworkers described many syntheses and applications of triazaphosphorines [15–18]. We have previously developed access to 2-substituted-1,3,5,2-triazaphosphorines via the condensation of trivalent or tetravalent phosphorus derivatives with compounds bearing two nucleophilic sites in 1,5-positions [19–21]. In this paper, we report the synthesis of new families of triazaphosphorines by condensation of *N*-thioamido amidines with phosphoramide derivatives and their oxidation by elemental sulfur.

RESULTS AND DISCUSSION

Synthesis of 1,3,5,2-Triazaphosphorines

Tris(dimethylamino)phosphine and bis(diethylamino)phenylphosphine are much less reactive than halogenated phosphorus derivatives such as phosphorus trichloride and phosphorus oxytrichloride. The conversion of phosphoramides requires more drastic conditions such as refluxing for several hours in high boiling solvents such as toluene or xylene, to effect cyclization reaction with compounds bearing two nucleophilic sites in 1,4- or

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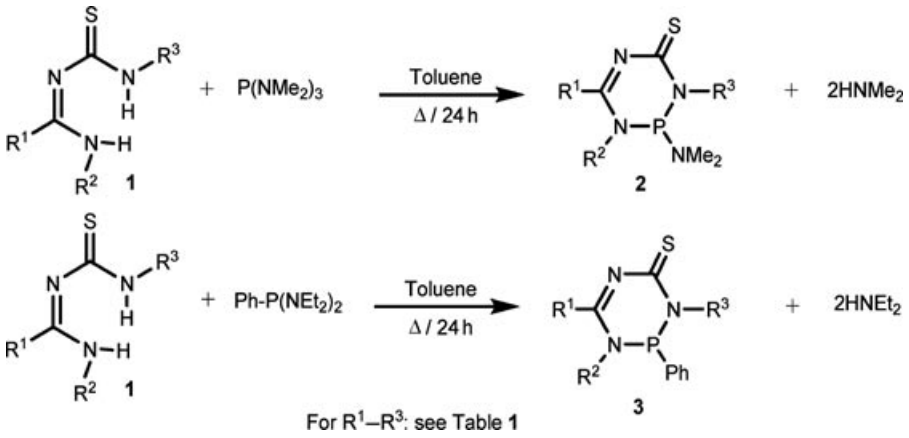


SCHEME 1

1,5-positions [21,22]. On the other hand, this kind of reaction, i.e. when hexamethylphosphoramide or bis(diethylamino)phenylphosphine are used in excess, gives pure products, whereas the use of halogenated phosphorus derivatives require more steps to separate the desired product from the hydrochloride salt. Only the release of dialkylamine gas was detected during the course of the reaction. The end of the reaction could easily be monitored by ^{31}P NMR spectroscopy or simply by testing the decrease of the evolution of dialkylamine gas using a pH paper.

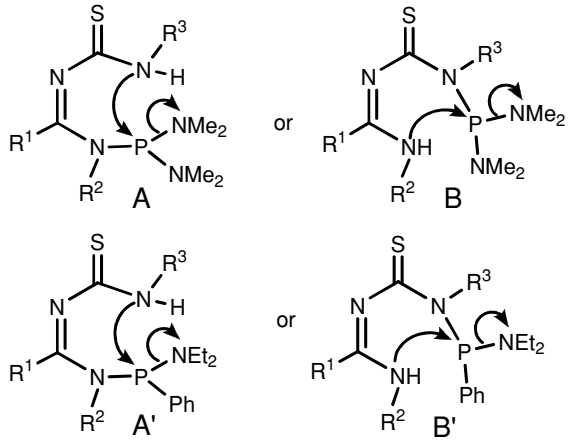
When the starting *N*-thioamido amidines **1** [23–25] are refluxed in anhydrous toluene with a small excess of tris(dimethylamino)phosphine or bis(diethylamino)phenylphosphine, the reaction leads to the corresponding 2-dimethylamino-1,3,5,2λ^3-triazaphosphorines **2** and 2-phenyl-1,3,5,2λ^3-triazaphosphorines **3**, respectively (Scheme 1). During the reaction for each compound, the ^{31}P NMR spectra show essentially two major signals at $\delta = 122$ ppm and $\delta = 70$–80 ppm or $\delta = 100$ ppm (Ph) and $\delta = 70$–80 ppm (Table 1); the two highest chemical shifts ($\delta = 122$ and 100 ppm) are attributed to the starting phosphoramide derivatives ($P(NMe_2)_3$ or $PhP(NEt_2)_2$), and the third one is assigned to the corresponding cyclic products **2** and **3**. The reaction is completed after heating the mixture for 22–24 h. Thus all reaction mixtures are refluxed for 24 h, followed by a standard workup.

The different products are summarized in Table I. The reaction yield depends strongly on the steric hindrance caused by the R^2 and R^3 moieties, i.e. the yield increases by decreasing of strain (R^3 = phenyl to benzyl to ethyl, when R^2 = benzyl). The final oily product could easily be purified by washing several times with small amounts of petroleum ether.

The reaction presumably proceeds via the formation of two possible intermediates **A** (**A′**) and **B** (**B′**) (Scheme 2). The first is obtained by phosphorylation

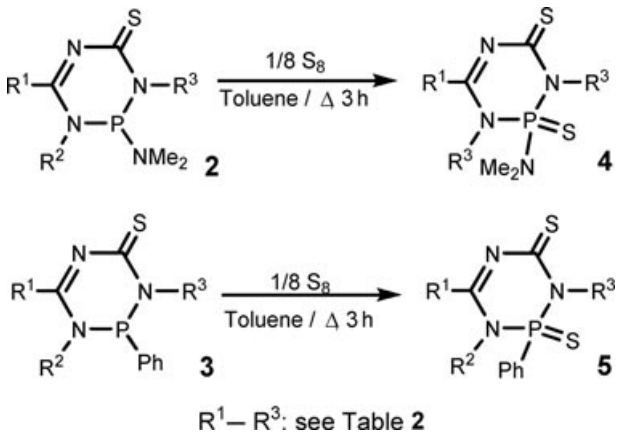
TABLE 1 Triazaphosphorines **2** and **3**

Compound	*R^1*	*R^2*	*R^3*	*^{31}P NMR*
2a	Ph	Bn	Bn	78.6
2b	Bn	Bn	Bn	81.4
2c	Ph	CH_3—CH—Ph	Bn	73.8
2d	Ph	Bn	Et	77.2
2e	Ph	CH_2—C_5H_4N	Ph	81.4
2f	Bn	Bn	Ph	81.5
3a	Ph	CH_3—CH—Ph	Bn	77.4
3b	Bn	Bn	Ph	81.0
3c	Bn	Bn	Bn	70.9
3d	Ph	Bn	Ph	77.3



R^1– R^3: see Table 1

SCHEME 2



SCHEME 3

TABLE 2 Triazaphosphorine-2-thiones **4** and **5**

Compound	*R^1*	*R^2*	*R^3*	*^{31}P NMR*
4a	Ph	Bn	Bn	58.5
4b	Bn	Bn	Bn	56.8
4c	Ph	CH_3—CH—Ph	Bn	63.8
4d	Ph	Bn	Et	57.9
4e	Ph	CH_2—C_5H_4N	Ph	59.3
4f	Bn	Bn	Ph	58.5
5a	Ph	CH_3—CH—Ph	Bn	61.1
5b	Bn	Bn	Ph	59.3
5c	Bn	Bn	Bn	59.6
5d	Ph	Bn	Ph	60.0

of the amidinic nitrogen atom and the second one by reaction of the thioamidinic nitrogen atom and $P(NMe_2)_3$ or Ph-$P(NEt_2)_2$. This is followed by a second intramolecular nucleophilic substitution of the dialkylamine to furnish the final products **2** and **3**.

AM1 and PM3 semiempirical calculations of the charges at different nitrogen atoms show that the electron density at the amidinic nitrogen atom, to which R^2 is linked, is higher than at the thioamidinic nitrogen atom, to which R^3 is linked and which is conjugated to the thiocarbonyl function. It is, therefore, more likely that the intermediate **A** (**A′**) is formed during this reaction, although the formation of intermediate **B** (**B′**) cannot be totally excluded.

Synthesis of 1,3,5,2-Triazaphosphorine-2-thiones

Heating the triazaphosphorines **2** and **3** in toluene for 3 h in the presence of a small excess of elemental sulfur leads to the corresponding 1,3,5,2λ^4-triazaphosphorine-2-thiones **4** and **5**, respectively (Scheme 3).

The ^{31}P NMR spectra show a shift to higher field of about 20 ppm, compared to that observed for the initial products (Table 2). The ^1H and ^{13}C NMR spectra do not reveal any significant changes with respect to the data of the starting compounds.

Spectroscopic Studies

IR Spectroscopy. The IR spectra of the starting amidines **1** show two characteristic bands at about 3200 and 3430 cm^{-1} related to the stretching vibrations of the two amidinic N—H bonds, and two other bands, the first at 1190 cm^{-1} due to the C=S vibration and the second one in the region of 1620–1660 cm^{-1} assigned to the stretching vibration of the C=N function. The IR spectra of the final products **2** and **3** do not display any band in the region between 3200 and 3400 cm^{-1}. The other bands show no major difference as compared to those of the starting compounds. However, the spectra reveal the presence of a new sharp, intense band at 1235 cm^{-1}, attributed to the P—N bond.

NMR Spectroscopies. The ^1H NMR spectra confirm the absence of the proton signals of the N—H functions and the presence of those related to the dimethylamino group introduced by the phosphorus substrate. In addition, a peak splitting due to phosphorus–proton coupling $^3J_{PH}$ (^3J = 10–11 Hz) when R^2 and/or R^3 = benzyl is observed. These observations are confirmed by ^{13}C NMR spectroscopy. All ^{31}P NMR spectra show a signal about 70–80 ppm, assigned to λ^3-P, which is in agreement with the literature and confirmed by our previous work [19–20]. The sulfuration of the products **2** and **3** by addition of elemental sulfur shifted the ^{31}P signal to higher field ($\delta = 60$ ppm). No major changes are detected in the ^1H or ^{13}C NMR spectra.

Mass Spectra. Owing to the low stability of the triazaphosphorines **2** and **3** in the ionization medium, the CI-MS spectra do not show the molecular M^+ peaks. The oxidation by sulfur addition stabilizes the products **4** and **5**, and $(M + H)^+$ is detected as the base peak. Moreover, the spectra of triazaphosphorines and triazaphosphorine-2-thiones reveal the existence of some common fragments such as $(M—R^2—NCS)^+$ or $(M—R^3)^+$ and some other phosphorus-containing moieties such as S=C—NHPh—P—$N(CH_3)_2$ or Ph—CH_2—N=P—Ph.

CONCLUSION

In this paper, a short and straightforward synthesis of 2-substituted-1,3,5,2-triazaphosphorines from *N*-thioamido amidines and phosphoramide derivatives is described. The derivatization of these compounds is possible through oxidation with elemental sulfur.

EXPERIMENTAL

Melting points were determined in open capillaries with an Electrothermal 9100 apparatus and are uncorrected. NMR spectra were recorded on a Bruker AC 300 spectrometer at 300 MHz (^{1}H), 75 MHz (^{13}C), and 121 MHz (^{31}P). Chemical shifts are given in ppm, using TMS as an internal standard for the ^{1}H and ^{13}C NMR and 85% H_3PO_4 as an external standard for ^{31}P NMR spectra. The IR spectra were recorded on a Perkin–Elmer Paragon 1000 spectrophotometer as $CHCl_3$ solution in the range 4000–400 cm^{-1}. CI-MS spectra were recorded on a JOEL MX 700 at ENS Paris. Elemental analyses were conducted by the Service de Microanalyse, CNRS at Gif-sur-Yvette, France.

N-thioamido imidines **1** were synthesized according to the literature [26], and the purity of the products was checked by the comparison of the melting point and by ^{1}H and ^{13}C NMR spectroscopy. Bis(diethylamino)phenylphosphine was obtained following the literature from aminolysis of commercial dichlorophenylphosphine; the product was collected by distillation, and purity was verified by ^{1}H and ^{31}P NMR spectroscopies [27].

Synthesis of the Dimethylamino-1,3,5,2-triazaphosphorines **2** *and* **3**

A mixture of 5.0 mmol of the *N*-thioamido amidine **1** and 5.5 mmol of tris(dimethylamino)phosphine in 20 mL of anhydrous toluene was heated to reflux in a nitrogen atmosphere for 24 h. The solvent was then evaporated under reduced pressure, and the resulting oily product was washed three times with 20 mL of petroleum ether to remove the excess of tris(dimethylamino)phosphine; the product was then heated (70°C) to dryness under reduced pressure (18 mmHg).

2a: Oil. Yield: 65%. IR ($CHCl_3$ solution 0.01 M): 3109 (ν_{C-H}), 1642 ($\nu_{C=N}$), 1227 (ν_{P-N}), 1179 ($\nu_{C=S}$) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.48 (d, 6H, $J = 11.1$ Hz, C$\underline{H}_3$—N); 4.41 (d, 2H, $J = 8.0$ Hz, C$\underline{H}_2$—N); 4.54 (d, 2H, $J = 6.4$ Hz, C$\underline{H}_2$—N); 6.88–7.89 (m, $\underline{H}_{arom}$); ^{13}C NMR (75 MHz, $CDCl_3$): δ 38.6 (N—$\underline{C}H_3$); 54.8 ($\underline{C}H_2$—N); 57.3 ($\underline{C}H_2$—N); 127.0; 128.4; 128.6; 128.8; 130.9; 137.2; 157.7 ($\underline{C}$=N); 188.6 ($\underline{C}$=S); ^{31}P NMR (121 MHz, $CDCl_3$): δ 78.6.

2b: Oil. Yield: 59%. IR ($CHCl_3$ solution 0.01 M): 3113 (ν_{C-H}), 1596 ($\nu_{C=N}$), 1235 (ν_{P-N}), 1188 ($\nu_{C=S}$) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.23 (d, 6H, $J = 10.4$ Hz, C$\underline{H}_3$—N); 2.77 (d, 2H, $J = 8.0$ Hz, C$\underline{H}_2$—C); 4.17 (d, 2H, $J = 7.1$ Hz, C$\underline{H}_2$—N); 4.54 (d, 6H, $J = 6.8$ Hz, C$\underline{H}_2$—N); 6.91–8.08 (m, $\underline{H}_{arom}$); ^{13}C NMR (75 MHz, $CDCl_3$): δ 36.7 (N—$\underline{C}H_3$); 41.4 ($\underline{C}H_2$—C); 45.6 ($\underline{C}H_2$—N); 48.6 ($\underline{C}H_2$—N); 125.6; 126.9; 129.1; 135.1; 140.4 C; 158.5 ($\underline{C}$=N); 181.9 ($\underline{C}$=S); ^{31}P NMR (121 MHz, $CDCl_3$): δ 81.4. Anal. Calcd for $C_{25}H_{27}N_4PS$(446): H: 6.09; C: 67.24; N: 12.55; Found: H: 6.15; C: 67.29; N: 12.57.

2c: Oil. Yield: 54%. IR ($CHCl_3$ solution 0.01 M): 3105 (ν_{C-H}), 1598 ($\nu_{C=N}$), 1237 (ν_{P-N}), 1184 ($\nu_{C=S}$) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.20 (t, 3H, $J = 7.0$ Hz, C$\underline{H}_3$—CH); 2.33 (d, 6H, $J = 10.4$ Hz, C$\underline{H}_3$—N); 4.19 (q, 2H, $J = 7.7$ Hz, C$\underline{H}$—N); 4.85 (d, 2H, $J = 7.3$ Hz, CH_2—N); 6.71–8.03 (m, $\underline{H}_{arom}$); ^{13}C NMR (75 MHz, $CDCl_3$): δ 38.6 (N—$\underline{C}H_3$); 54.8 ($\underline{C}H_2$—N); 59.3 ($\underline{C}$H—N); 126.4; 128.2; 129.4; 129.9; 133.1; 136.7; 158.9 ($\underline{C}$=N); 192.5 ($\underline{C}$=S); ^{31}P NMR (121 MHz, $CDCl_3$): δ 73.8. Anal. Calcd for $C_{25}H_{27}N_4PS$ (446): H: 6.09; C: 67.24; N: 12.55; Found: H: 6.01; C: 67.13; N: 12.60.

2d: Oil. Yield: 53%. IR ($CHCl_3$ solution 0.01 M): 3109 (ν_{C-H}), 1592 ($\nu_{C=N}$), 1236 (ν_{P-N}), 1186 ($\nu_{C=S}$) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.33 (t, 3H, $J = 6.8$ Hz, C$\underline{H}_3$—CH_2); 2.24 (d, 6H, $J = 10.5$ Hz, CH_3—N); 3.37 (q, 2H, $J = 6.8$ Hz, C$\underline{H}_2$—CH_3); 4.51 (d, 2H, $J = 7.1$ Hz, C$\underline{H}_2$—N); 7.05–7.93 (m, $\underline{H}_{arom}$); ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.2 ($\underline{C}H_3$—CH_2); 37.6 (N—$\underline{C}H_3$); 44.6 ($\underline{C}H_2$—CH_3); 57.3 ($\underline{C}H_2$—N); 125.7; 127.6; 127.8; 129.9; 132.4; 137.2; 157.3 ($\underline{C}$=N); 189.9 ($\underline{C}$=S); ^{31}P NMR (121 MHz, $CDCl_3$): δ 77.2. Anal. Calcd for $C_{19}H_{23}N_4PS$ (370,5): H: 6.21; C: 61.60; N: 15.12; Found: H: 6.35; C: 61.73; N: 15.24.

2e: Oil. Yield: 58%. IR ($CHCl_3$ solution 0.01 M): 3114 (ν_{C-H}), 1599 ($\nu_{C=N}$), 1232 (ν_{P-N}), 1189 ($\nu_{C=S}$) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.57 (d, 6H, $J = 11.0$ Hz, C$\underline{H}_3$—N); 4.61 (d, 2H, $J = 8.0$ Hz, C$\underline{H}_2$—N); 7.15–8.08 (m, $\underline{H}_{arom}$); ^{13}C NMR (75 MHz, $CDCl_3$): δ 37.9 (N—$\underline{C}H_3$); 57.3 ($\underline{C}H_2$—N); 126.7; 127.6; 128.4; 129.1; 136.5; 155.5 ($\underline{C}$=N); 193.1 ($\underline{C}$=S); ^{31}P NMR (121 MHz, $CDCl_3$): δ 81.4. MS (CI, NH_3): *m/z* (%) = 420 (100) [M^+ + H]; 419; 211 (45) [S=C—NHPh—P—N$(CH_3)_2]^+$.

2f: Oil. Yield: 51%. IR ($CHCl_3$ solution 0.01 M): 3106 (ν_{C-H}), 1591 ($\nu_{C=N}$), 1238 (ν_{P-N}), 1190 ($\nu_{C=S}$) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.61 (d, 6H, $J = 10.7$ Hz, C$\underline{H}_3$—N); 3.84 (d, 2H, $J = 6.1$ Hz, C$\underline{H}_2$—C); 4.48 (d, 2H, $J = 8.5$ Hz, C$\underline{H}_2$—N); 7.11–7.84 (m, $\underline{H}_{arom}$). ^{13}C NMR (75 MHz, $CDCl_3$): δ 38.3 (N—$\underline{C}H_3$); 55.3 ($\underline{C}H_2$—N); 57.8 ($\underline{C}H_2$—N); 126.8; 127.5;

128.6; 129.3; 134.1; 139.7; 159.2 (C=N); 193.6 (C=S); ^{31}P NMR (121 MHz, $CDCl_3$): δ 81.5. Anal. Calcd For $C_{24}H_{25}N_4PS$ (432): H: 5.83; C: 66.65; N: 12.95; Found: H: 5.91; C: 66.72; N: 13.01.

Synthesis of the Phenyl-1,3,5,2-triazaphosphorines **3**

To a solution of *N*-thioamido amidine **1** (5.0 mmol) in 20 mL of anhydrous toluene, 5.5 mmol of phenyl(diethylamino)phosphine was added. The mixture was heated to reflux in a nitrogen atmosphere for 24 h. The solvent was then removed under reduced pressure, the resulting oily residue was washed three times with 20 mL of petroleum ether to remove excess of phenyl(diethylamino)phosphine; the product was dried under reduced pressure (18 mmHg).

3a: Oil. Yield: 69%. IR ($CHCl_3$ solution 0.01 M): 3107 (ν_{C-H}), 1598 ($\nu_{C=N}$), 1235 (ν_{P-N}), 1196 ($\nu_{C=S}$) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.22 (d, 3H, $J = 8.3$ Hz, C$\underline{H}_3$–CH); 4.21 (q, 1H, $J = 8.2$ Hz, CH_3–C$\underline{H}$); 4.58 (d, 2H, $J = 10.9$ Hz, C$\underline{H}_2$–N); 7.17–7.83 (m, $\underline{H}_{arom}$); ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.6 (C$\underline{H}_3$–CH); 42.7 (C$\underline{H}_2$–C); 65.8 (CH_3–C$\underline{H}$); 125.6; 126.8; 128.2; 130.9; 141.9; 142.2; 155.9 (C=N); 178.3 (C=S); ^{31}P NMR (121 MHz, $CDCl_3$): δ 77.4. Anal. Calcd for $C_{29}H_{26}N_3PS$ (479): H: 5.46; C: 72.63; N: 8.76; Found: H: 5.48; C: 72.87; N: 8.81.

3b: Oil. Yield: 60%. IR ($CHCl_3$ solution 0.01 M): 3111 (ν_{C-H}), 1597 ($\nu_{C=N}$), 1233 (ν_{P-N}), 1194 ($\nu_{C=S}$) cm^{-1}. ^{1}H NMR (300 MHz, DMSO-d_6): δ 3.57 (d, 2H, $J = 7.2$ Hz, C$\underline{H}_2$–C); 4.44 (d, 2H, $J = 8.4$ Hz, C$\underline{H}_2$–N); 6.49–8.43 (m, $\underline{H}_{arom}$); ^{13}C NMR (75 MHz, $CDCl_3$): δ 42.4 (C$\underline{H}_2$–C); 45.1 (C$\underline{H}_2$–N); 125.6; 126.9; 129.1; 129.5; 134.8; 139.9; 140.9; 154.5 (C=N); 183.9 (C=S); ^{31}P NMR (121 MHz, $CDCl_3$): δ 81.0. MS (CI, NH_3): *m/z* (%) = 465 (8) $[M]^+$; 225 (100) $[M - (Ph–N=C=S + Ph–CH=N)]^+$; 209 (37) $[Ph–CH_2–CH=N–CH_2–Ph]^+$.

3c: Oil. Yield: 63%. IR ($CHCl_3$ solution 0.01 M): 3112 (ν_{C-H}), 1594 ($\nu_{C=N}$), 1234 (ν_{P-N}), 1207 ($\nu_{C=S}$) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.22 (d, 2H, $J = 7.5$ Hz, C$\underline{H}_2$–C); 4.46 (d, 2H, $J = 7.4$ Hz, C$\underline{H}_2$–N); 4.65 (d, 2H, $J = 7.8$ Hz, C$\underline{H}_2$–N); 7.07–7.84 (m, $\underline{H}_{arom}$); ^{13}C NMR (75 MHz, $CDCl_3$): δ 42.4 (C$\underline{H}_2$–C); 45.1 (C$\underline{H}_2$–N); 48.1 (C$\underline{H}_2$–N); 127.1; 127.8; 128.4; 131.0; 136.6; 138.9; 154.5 (C=N); 183.9 (C=S); ^{31}P NMR (121 MHz, $CDCl_3$): δ 70.9.

3d: Oil. Yield: 69%. IR ($CHCl_3$ solution 0.01 M): 3115 (ν_{C-H}), 1587 ($\nu_{C=N}$), 1229 (ν_{P-N}), 1198 ($\nu_{C=S}$) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.73 (d, 2H, $J = 7.7$ Hz, C$\underline{H}_2$–N); 7.11–7.95 (m, $\underline{H}_{arom}$); ^{13}C NMR (75 MHz, $CDCl_3$): δ 46.5 (C$\underline{H}_2$–N); 125.5; 127.4; 129.2; 131.7; 133.5; 137.6, 139.3; 155.7 (C=N); 184.7 (C=S); ^{31}P NMR (121 MHz, $CDCl_3$): δ 77.3. MS (CI, NH_3): *m/z* (%) = 451 (8) $[M]^+$; 346 (40) $[M–N–CH_2–Ph]^+$; 211 (47) $[Ph–CH_2–N=P–Ph]^+$. Anal. Calcd for $C_{27}H_{22}N_3PS$ (451): H: 4.91; C: 71.82; N: 9.31; Found: H: 5.01; C: 72.05; N: 9.47.

Synthesis of the 2-Substituted-1,3,5,2-triazaphosphorine-2-thiones **4** *and* **5**

1.0 mmol of the 2-substituted-1,3,5,2-triazaphosphorine **2** or **3** was dissolved in 10 mL of anhydrous toluene, and 1.1 mmol of elemental sulfur was added. The mixture was heated to reflux for 3 h. After cooling, the solvent was evaporated under reduced pressure and 10 mL of anhydrous petroleum ether was added to the residue. A yellowish precipitate was formed; the solid was collected by filtration and was used as it was without further purification.

4a: mp: 116–118°C; Yield: 75%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.31 (d, 6H, $J = 10.7$ Hz, C$\underline{H}_3$–N); 4.57 (d, 2H, $J = 5.6$ Hz, C$\underline{H}_2$–N); 4.70 (d, 2H, $J = 9.2$ Hz, C$\underline{H}_2$–N); 6.59–7.94 (m, $\underline{H}_{arom}$); ^{13}C NMR (75 MHz, $CDCl_3$): δ 38.3 (N–C$\underline{H}_3$); 54.4 (C$\underline{H}_2$–N); 56.8 (C$\underline{H}_2$–N); 125.1–127.7; 129.7; 131.9; 133.3; 136.8; 158.6 (C=N); 187.2 (C=S); ^{31}P NMR (121 MHz, $CDCl_3$): δ 58.5. DCI-MS *m/z* (%) = 466 (32) $[M + H]^+$; 465 (100) $[M]^+$; 360 (60) $[M–N–CH_2–Ph]^+$.

4b: mp: 129–131°C; Yield: 59%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.33 (d, 6H, $J = 11.0$ Hz, C$\underline{H}_3$–N); 3.88 (d, 2H, $J = 6.9$ Hz, C$\underline{H}_2$–C); 4.51 (d, 2H, $J = 5.8$ Hz, C$\underline{H}_2$–N); 4.77 (d, 2H, $J = 9.2$ Hz, C$\underline{H}_2$–N); 6.33–7.97 (m, $\underline{H}_{arom}$); ^{13}C NMR (75 MHz, $CDCl_3$): δ 36.3 (N–C$\underline{H}_3$); 41.8 (C$\underline{H}_2$–C); 45.3 (C$\underline{H}_2$–N); 49.2 (C$\underline{H}_2$–N); 125.9; 127.2; 129.9; 138.3; 142.7; 159.3 (C=N); 186.4 (C=S); ^{31}P NMR (121 MHz, $CDCl_3$): δ 56.8.

4c: mp: 144–146°C; Yield: 54%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.23 (d, 3H, $J = 7.0$ Hz, C$\underline{H}_3$–CH); 2.34 (d, 6H, $J = 10.5$ Hz, C$\underline{H}_3$–N); 4.19 (q, 2H, $J = 7.0$ Hz, C$\underline{H}$–CH_3); 4.78 (d, 2H, $J = 6.2$ Hz, CH_2–N); 6.76–8.05 (m, $\underline{H}_{arom}$); ^{13}C NMR (75 MHz, $CDCl_3$): δ 27.2 (C$\underline{H}_3$–CH); 38.6 (C$\underline{H}_3$–N); 54.8 (C$\underline{H}_2$–N); 59.3 (C$\underline{H}$–CH_3); 124.5; 127.7; 128.3; 130.2; 134.6; 138.8; 161.5 (C=N); 196.2 (C=S); ^{31}P NMR (121 MHz, $CDCl_3$): δ 63.8.

4d: mp: 131–132°C; Yield: 78%; ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.42 (t, 3H, $J = 7.3$ Hz, C$\underline{H}_3$–CH_2); 2.33 (d, 6H, $J = 10.8$ Hz, CH_3–N); 3.48 (q, 2H, $J = 7.3$ Hz, C$\underline{H}_2$–CH_3); 4.64 (d, 2H, $J = 11.2$ Hz, C$\underline{H}_2$–N); 6.95–7.93 (m, $\underline{H}_{arom}$); ^{13}C NMR (75 MHz, $CDCl_3$): δ 16.6 (C$\underline{H}_3$–CH_2); 36.4 (N–C$\underline{H}_3$); 45.9 (C$\underline{H}_2$–CH_3); 58.7 (C$\underline{H}_2$–N); 124.2; 126.5; 127.6; 128.3; 135.1; 137.9; 158.4 (C=N); 192.2 (C=S); ^{31}P NMR (121 MHz, $CDCl_3$): δ 57.9. Anal. Calcd for $C_{19}H_{23}N_4PS_2$ (402): H:

5.72; C: 56.72; N: 13.93; Found: H: 5.85; C: 56.89; N: 14.06.

4e: mp: 127–129°C; Yield: 58%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.63 (d, 6H, $J = 10.3$ Hz, C$\underline{H}_3$—N); 4.62 (d, 2H, $J = 11.2$ Hz, C$\underline{H}_2$—N); 7.07–8.14 (m, $\underline{H}_{arom}$); ^{13}C NMR (75 MHz, $CDCl_3$): δ 36.3 (N—$\underline{C}H_3$); 55.7 ($\underline{C}H_2$—N); 124.4; 126.2; 127.0; 129.6; 138.7; 145.2; 158.9 ($\underline{C}$=N); 195.3 ($\underline{C}$=S); ^{31}P NMR (121 MHz, $CDCl_3$): δ 59.3.

4f: mp: 116–118°C; Yield: 68%; ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.61 (d, 6H, $J = 10.6$ Hz, C$\underline{H}_3$—N); 3.77 (d, 2H, $J = 6.6$ Hz, C$\underline{H}_2$—C); 4.75 (d, 2H, $J = 7.2$ Hz, C$\underline{H}_2$—N); 7.05–7.83 (m, $\underline{H}_{arom}$); ^{13}C NMR (75 MHz, $CDCl_3$): δ 36.5 (N—$\underline{C}H_3$); 46.5 ($\underline{C}H_2$—C); 58.1 ($\underline{C}H_2$—N); 126.2; 127.8; 129.2; 129.7; 133.4; 138.7; 144.8; 157.8 ($\underline{C}$=N); 191.9 ($\underline{C}$=S); ^{31}P NMR (121 MHz, $CDCl_3$): δ 58.5. Anal. Calcd for $C_{24}H_{25}N_4PS_2$(464): H: 5.38; C: 62.07; N: 12.06; S: 13.80; Found: H: 5.45; C: 61.89; N: 12.11; S: 13.73.

5a: mp: 114–115°C; Yield: 82%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.28 (d, 2H, $J = 10.8$ Hz, C$\underline{H}_3$—CH); 4.31 (q, 2H, $J = 10.8$ Hz, CH_3—C$\underline{H}$); 4.65 (d, 2H, $J = 7.2$ Hz, C$\underline{H}_2$—N); 7.02–7.88 (m, $\underline{H}_{arom}$); ^{13}C NMR (75 MHz, $CDCl_3$): δ 15.3 ($\underline{C}H_3$—CH); 54.1 ($\underline{C}H_2$—N); 67.5 (CH_3—$\underline{C}$H); 126.7; 128.4; 129.6; 131.5; 140.7; 145.0; 157.6 ($\underline{C}$=N); 185.7 ($\underline{C}$=S); ^{31}P NMR (121 MHz, $CDCl_3$): δ 61.1. MS (CI): m/z (%) = 285 (10) [Ph—P(S)—N—CH_2—Ph+2H]$^+$. Anal. Calcd for $C_{29}H_{26}N_3PS_2$(497): H: 5.09; C: 68.10; N: 8.22; S: 12.52; Found: H: 5.17; C: 68.23; N: 8.41; S: 12.73.

5b: mp: 124–125°C; Yield: 60%. ^{1}H NMR (300 MHz, DMSO-d_6): δ 3.92 (d, 2H, $J = 6.7$ Hz, C$\underline{H}_2$—C); 4.44 (d, 2H, $J = 7.3$ Hz, C$\underline{H}_2$—N); 6.49–8.43 (m, $\underline{H}_{arom}$); ^{13}C NMR (75 MHz, $CDCl_3$): δ 44.2 ($\underline{C}H_2$—C); 47.7 ($\underline{C}H_2$—N); 124.3; 126.9; 129.8; 130.2; 134.8; 141.5; 144.2; 157.7 ($\underline{C}$=N); 188.2 ($\underline{C}$=S); ^{31}P NMR (121 MHz, $CDCl_3$): δ 59.3.

5c: mp: 114–116°C; Yield: 72%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.63 (d, 2H, $J = 6.5$ Hz C$\underline{H}_2$—C); 4.35 (d, 2H, $J = 7.4$ Hz, C$\underline{H}_2$—N); 4.49 (d, 2H, $J = 7.0$ Hz, C$\underline{H}_2$—N); 7.01–7.94 (m, $\underline{H}_{arom}$); ^{13}C NMR (75 MHz, $CDCl_3$): δ 42.7 ($\underline{C}H_2$—C); 46.3 ($\underline{C}H_2$—N); 48.4 ($\underline{C}H_2$—N); 125.3; 128.8; 129.4; 133.1; 138.8; 140,1; 157.3 ($\underline{C}$=N); 185.7 ($\underline{C}$=S); ^{31}P NMR (121 MHz, $CDCl_3$): δ 59.6. MS (CI): m/z (%) = 271(31) [Ph—$CH(CH_3)$—NH—P(S)—Ph]$^+$.

5d: mp: 131–133°C; Yield: 69%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.78 (d, 2H, $J = 7.4$ Hz, C$\underline{H}_2$—N); 7.11–7.95 (m, $\underline{H}_{arom}$); ^{13}C NMR (75 MHz, $CDCl_3$): δ 49.7 ($\underline{C}H_2$—N); 122.7; 124,1; 127.4; 128.8; 130.5; 133.9; 137.5, 140.2; 159.5 ($\underline{C}$=N); 189.3 ($\underline{C}$=S); ^{31}P NMR (121 MHz, $CDCl_3$): δ 60.0. MS (CI, NH_3): m/z (%) = 484 (100) [M + H]$^+$; 211 (47) [Ph—CH_2—N=P—Ph]$^+$. Anal. Calcd for $C_{28}H_{24}N_3PS_2$(483): H: 4.55; C: 67.08; N: 8.69; Found: H: 4.73; C: 67.22; N: 8.79.

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