EurJIC
European Journal of Inorganic Chemistry

A Journal of ChemPubSoc Europe

Accepted Article

Title: A straightforward synthesis of 1,2-azaphosphindoles

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To be cited as: *Eur. J. Inorg. Chem.* 10.1002/ejic.201700209

Link to VoR: http://dx.doi.org/10.1002/ejic.201700209

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A Straightforward Synthesis of 1,2-Azaphosphindoles

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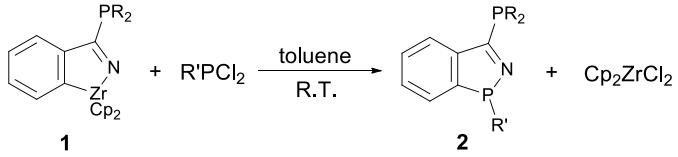
Treatment of *ortho*-(diphenylphosphino)phenyl nitriles with an excess of lithium at room temperature in THF gives 1,2-azaphosphindolides, which can react with RX (benzyl bromide, 1-bromopropane and 1,2-dibromoethane) to form 2*H*-1,2-azaphosphindoles and give the aromatic 1*H*-1,2-azaphosphindoles upon protonation.

Introduction

Compared with the well-known benzo-fused 1,3-azaphospholes[1], there has been a noticeable absence of 1,2-azaphosphindoles (phosphorus analogues of indoles) in the literature. The first 1,2-azaphosphindoles were reported by Majoral as early as 2000[2], no other synthetic route to these species has ever been mentioned in the literature after that. The reaction involves an exchange of zirconium for phosphorus (Scheme 1). Likewise, there has been scant mention in the literature of the chemistry of 1,2-azaphosphindolides.

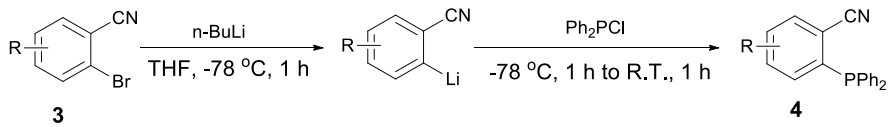


Scheme 1. Synthesis of 1,2-azaphosphindoles

Very recently, our group developed a new method to synthesize phosphindoles and 1,3-benzazaphospholes by treatment of open-chain acetylenic phosphines[3] and *ortho*-(diarylphosphino)aryl isocyanides[4]with an excess of lithium, followed by alkylation at phosphorus with benzyl bromide or methyl iodide. In view of the potentially synthetic and coordination chemistry of 1,2-azaphosphindoles, it was tempting to generalize this kind of approach to prepare these species by a new and simple route involving the reaction of easily made *ortho*-(diphenylphosphino)phenyl nitriles with lithium.

Results and discussion

Our substrates **4a-c** were easily obtained by reaction of 2-lithiophenyl nitriles with diphenylchlorophosphines in good to excellent yields as shown in Scheme 2.

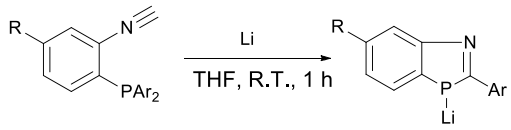


4a: R= *m*-H, 76 %
4b: R= *m*-Me, 88 %
4c: R= *p*-OMe, 53%

Scheme 2. Synthesis of *ortho*-(diphenylphosphino)phenyl nitriles

The ^{31}P resonance of phosphines **4** are found at -8.3 (**4a**), -9.9 (**4b**), and -7.9 ppm (**4c**) in $CDCl_3$ which shows a shielding when compared to triphenylphosphine ($\delta^{31}P$ = -6 ppm). The ^{13}C spectrum of phosphine-nitriles display a CN

resonance between 116.39 and 118.03 ppm. Compounds **4** have two reactive centers (P and CN) as do *o*rtho-(diarylphosphino)aryl isocyanides which formed the 1,3-azaphospholides **6** with an excess of lithium at room temperature in THF (Scheme 3).

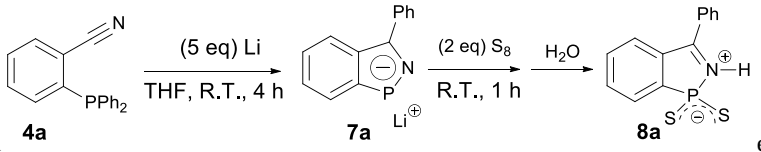


5 **6**

6a R=H, Ar=Ph
6b R=Me,Ar=Ph
6c R=H, Ar= *para*-Tol

Scheme 3. Synthesis of 1,3-azaphospholides **6**

In view of this report, we decided to investigate the reaction of lithium with our substrates **4a-c**. Since the intramolecular nucleophilic attack of nitrile group will give a 4-membered ring, we expected that the cyclization reaction would be difficult than isocyanide case. Unexpectedly, the reaction of compound **4a** with lithium in anhydrous THF took place at room temperature and monitoring the reaction medium by ^{31}P NMR spectroscopy showed a new signal at δ = 165.0 ppm (besid



4a **7a** **8a**

es some Ph_2PLi, at δ = -20.7 ppm) . In order to more fully establish the formula of the azaphospholide, we quenched it by reaction with sulfur and obtained the pure dithiophosphinate **8a** after column chromatography on silica gel. Compound **8a** was characterized by X-ray crystal structure analysis.

The structure of **8a** is shown in Figure 1, the P1-N1 (1.7851(19) Å) and N1-C7 (1.301(3)Å) bond lengths correspond to P-N single bond and N-C double bond. Both of P-S bond lengths are almost same. The other representative bond lengths and angles are in good agreement with the numerous data reported in the literature[2,5,6].

Scheme 4. Synthesis of the 1,2-azaphosphindoledisulfide **8a**

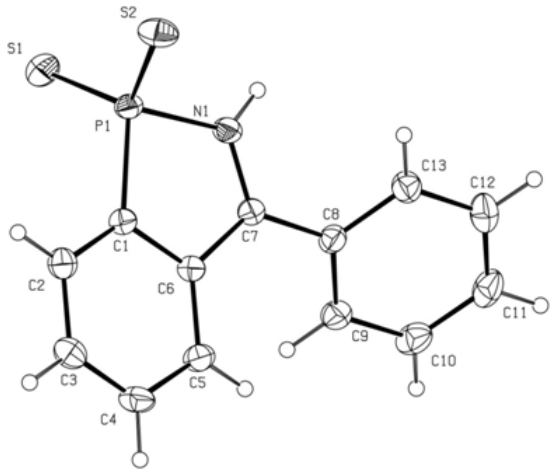
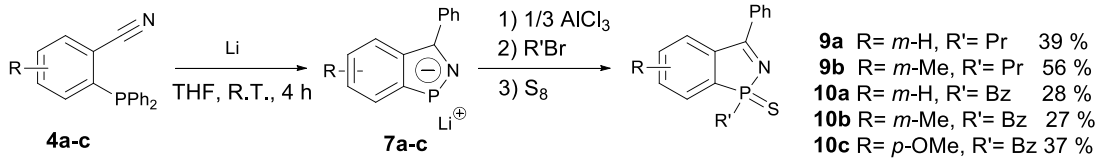


Figure 1: ORTEP drawing of 1,2-azaphosphindoledisulfide **8a** (30% thermal ellipsoids). Main distances (Å) and angles (deg.): S1-P1 1.9394(10), S2-P1 1.9521(9), P1-N1 1.7851(19), P1-C1 1.815(2), N1-C7 1.301(3),C1-C6 1.402(3), C6-C7 1.465(3); S1-P1-S2 121.25(4), N1-P1-S1 107.60(8), N1-P1 -S2 107.95(8), N1-P1-C1 87.48(10), C1-P1-S1 113.62(8), C1-P1-S2113.16(8).

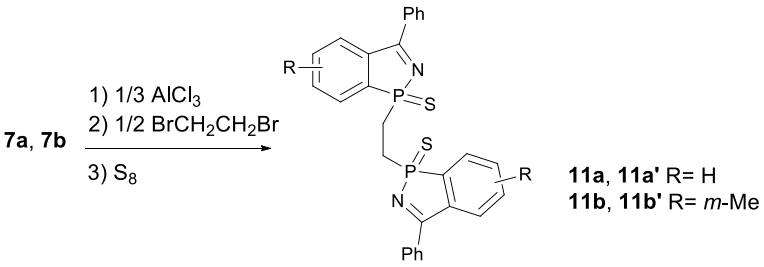
Thus, the first reported 1,2-azaphosphindolide **7a** was formed (Scheme 4) in one-step from a readily accessible starting material. To study its reactivity, treating **7a** with 1-bromopropane or benzyl bromide and sulfur gave benzo-1,2-

azaphosphole (or 1,2-azaphosphindole) sulfides **9a** and **10a**. Similar results were obtained with **4b** and **4c** (Scheme 5). Side products Ph_2PR' were observed also.



Scheme 5. Synthesis of 1,2-azaphosphindole sulfides

Besides, the reaction of azaphospholides **7a** and **7b** with 1,2-dibromoethane and sulfur afforded the expected bis-1,2-azaphosphindole disulfides (Scheme 6) in 62 % and 60 % yields as inseparable mixtures of two diastereoisomers[2] **11a**, **11a'** (^{31}P NMR 88.01, 87.88 ppm respectively, in a ratio of *ca.* 1:1.3) and **11b**, **11b'**(^{31}P NMR 87.65, 87.47 ppm respectively, in a ratio of *ca.* 1:1.6).



Scheme 6. Synthesis of bis(1,2-azaphosphindole) disulfides

The literature on the closely related 1,3-benzazaphospholes reports that the 1,3-benzazaphospholides are alkylated at phosphorus but protonated at nitrogen.[1c,7] Thus, we decided to study the protonation of 1,2-azaphosphindolide **7a** from a theoretical standpoint. The computations were carried out by DFT at the B3LYP/6-311+G(d,p) level.[8] The computed structure of **7a** is shown in fig. (2).

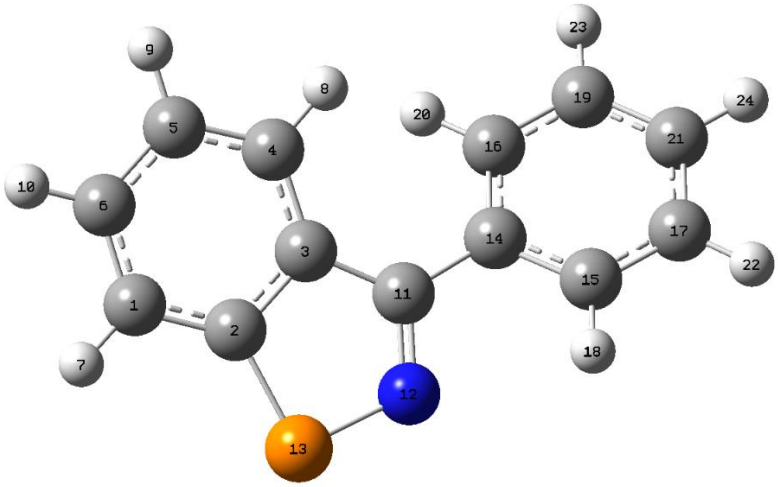


Figure 2: Computed structure of 1,2-azaphosphindolide **7a**. Main bond distances (À) and angles (deg.): P-N 1.683, P-C2 1.786, C2-C3 1.440, C3-C11 1.443, C11-N 1.340; C2-P-N 92.32, P-C2-C3 108.94, C2-C3C11 110.18, C3-C11-N 114.73, C11-N-P 113.79.

The azaphosphindole ring is strictly planar and the phenyl substituent is tilted out of this plane by 26.15 deg. The azaphosphindolide can be protonated at N to give **12a**. The computed structure is shown in fig. (3).

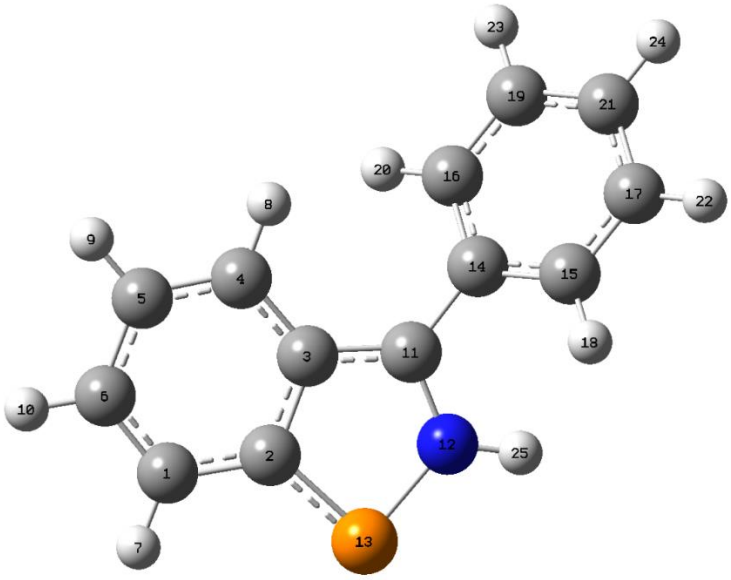


Figure 3: Computed structure of 1*H*-1,2-azaphosphindole **12a**. Main bond distances (À) and angles (deg.): P-N 1.728, P-C2 1.759, C2-C3 1.440, C3-C11 1.412, C11-N 1.358; C2-P-N 87.74, P-C2-C3 112.38, C2-C3-C11 111.71, C3-C11-N 110.29, C11-N-P 117.87.

The structure is almost non-affected by the protonation, the ring remains strictly planar, the nitrogen atom is flat. The shape of the HOMO (fig.4) shows that **12a** can be legitimately considered as a 10π aromatic system. Such species are quite rare in the literature.[9]

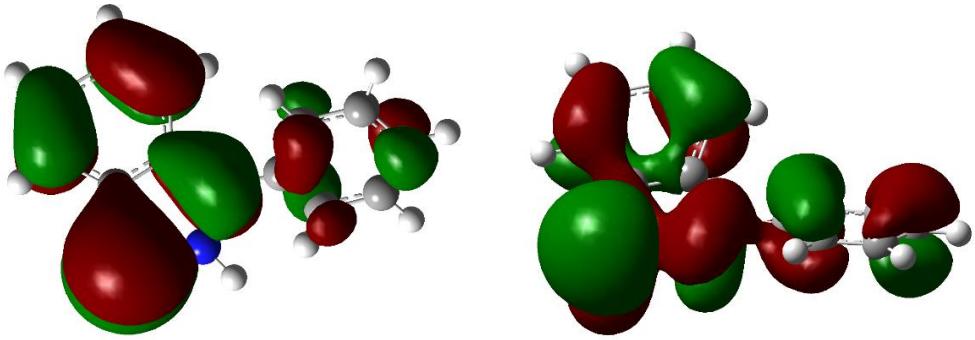


Figure 4: HOMO's of 1*H* and 2*H*-1,2-azaphosphindoles **12a** and **13a** (Kohn-Sham).

The protonation of the 1,2-azaphosphindolide at phosphorus would afford **13a** whose computed structure is shown in fig.(5).

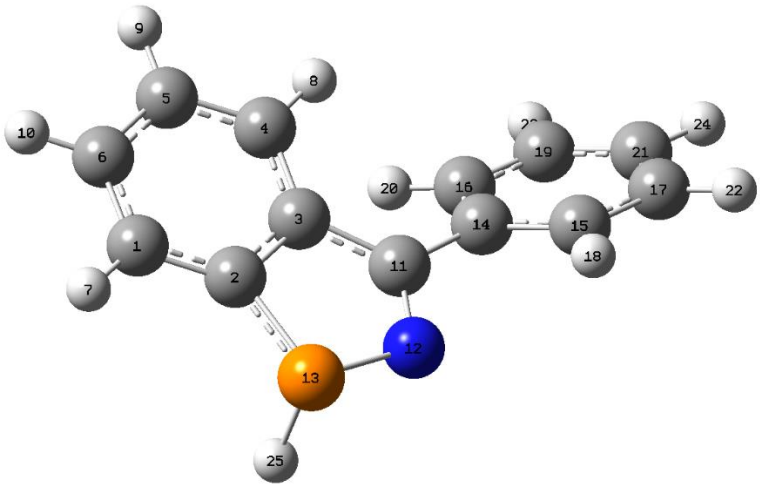
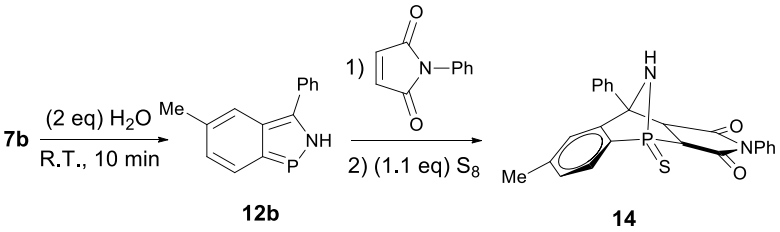


Figure 5: Computed structure of 2*H*-1,2-azaphosphindole **13a**. Main bond distances (À) and angles (deg.): P-N 1.738, P-C2 1.833, C2-C3 1.410, C3-C11 1.484, C11-N 1.295; C2-P-N 92.43, P-C2-C3 107.26, C2-C3-C11 111.06, C3-C11-N 116.74, C11-N-P 111.68.

The molecule is not planar, the phosphorus atom is pyramidal (Σangles at P = 290.4 deg.), the P-C bond is quite long at 1.833 À and the HOMO (fig.4) is strongly localized at P and N. The system is not any more aromatic. As a consequence, **13a** is less stable than **12a** by 12.0 kcal mol^{-1}. Thus, this theoretical study clearly predicts that the protonation of azaphosphindolide **7a** will ultimately give the NH derivative. Of course, initial protonation at P, followed by a [1,2]-shift of H from P to N is quite possible. The situation is quite similar when phospholes (pyramidal at P and non-aromatic) are compared with pyrroles (planar at N and aromatic).[10]



Scheme 7. Synthesis of compound **14**

We detected the formation of **12b** (^{31}P MNR 157 ppm) by treating azaphosphindolide **7b** with water. But its reactivity precluded its isolation. We trapped it by reaction with N-phenylmaleimide and sulfur as shown in Scheme 7. Compound **14** has been characterized by X-ray crystal structure analysis (Figure 6).

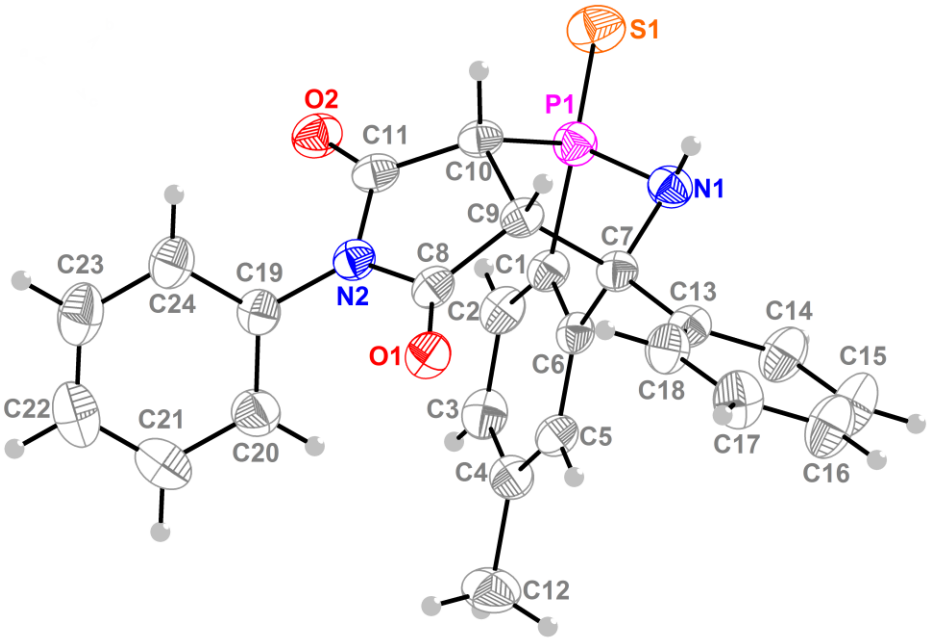


Figure 6: ORTEP drawing of compound **14** (30% thermal ellipsoids). Main distances (Å) and angles (deg.): C1-P1 1.792(3), C10-P1 1.863(3), N1-P1 1.686(3), S1-P1 1.9172(12), C9-C10 1.548(4), C7-C9 1.594(4), C1-C6 1.399(4), C6-C7 1.530(4); C1-P1-C10 97.34(13), N1-P1-C1 90.69(14), N1-P1-C10 94.62(13), C7-N1-P1 100.5(2).

Conclusion

In conclusion, the first 1,2-azaphosphindolides were prepared and their reactivity toward several kinds of electrophiles was preliminarily studied. Their alkylation at P provides a simple route to 1,2-azaphosphindoles. Their protonation affords NH isomers that display a 10π aromaticity. Coordination chemistry and other applications of these species are under further investigation.

Experimental section

All reactions were performed under nitrogen using solvents dried by standard methods. ^{1}H, ^{13}C and ^{31}P NMR spectra were recorded on Bruker 300 MHz spectrometer. Chemical shifts are expressed in ppm from internal TMS (^{1}H and^{13}C). All coupling constants (*J* values) are reported in hertz (Hz). HRMS spectra were obtained on a Water Q- Tof Premier MS. Element analytic data were obtained on a Thermo Electron Corporation flash EA 1112 element spectrometer. Silica gel (230- 400 mesh) was used for the chromatographic separations. Commercially available reagents were used without further purification.

*Procedure A for Synthesis of the Starting Phosphines **4a**-**4c**:*

To a solution of *ortho*-bromoaryl nitriles (30 mmol) in anhydrous THF (60 mL), kept in an oven-dried 100 mL-Schlenk flask under an atmosphere of dry nitrogen, was added dropwise a 1.6 M solution of *n*-BuLi in hexane (18.8 mL, 30 mmol) at –78 °C over a period of 5 min. After stirring at –78 °C for 1 h, Ph_2PCl (6.62 g, 30 mmol) in anhydrous THF (10 mL) was added dropwise. The mixture was kept at –78 °C for 1 h and then warmed to room temperature. After 1h, the reaction was monitored by ^{31}P NMR spectroscopy. The mixture was diluted with diethyl ether, the organic phase washed with water, brine and dried over anhydrous $MgSO_4$. The solvents were removed under reduced pressure to give a crude product, which was purified by column chromatography on silica gel (petroleum ether/ dichloromethane).

*Phosphine **4a***

White solid, 6.55 g, 76 % yield. ^{31}P NMR (121 MHz, $CDCl_3$): δ -8.3 ppm; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.06-7.10 (m, 1H), 7.27-7.51 (m, 12H), 7.70-7.74 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 117.66 (d, J_{CP} = 3.8 Hz, CN), 117.93 (d, J_{CP} = 33.0 Hz, C), 128.88 (d, J_{CP} = 7.5 Hz, 4CH), 128.93 (s, CH), 129.48 (s, 2CH), 132.47 (s, CH), 133.45 (s, CH), 133.76 (d, J_{CP} = 4.5 Hz, CH),

134.05 (d, J_{CP} = 20.3 Hz, 4CH), 134.70 (d, J_{CP} = 10.5 Hz, 2C), 143.03 (d, J_{CP} = 20.3 Hz, C). HRMS: m/z calcd. for $C_{19}H_{15}NP$ $[M+H]^+$: 288.0942; found : 288.0945.

*Phosphine **4b***

White solid, 7.92 g, 88 % yield. ^{31}P NMR (121 MHz, $CDCl_3$): δ-9.9 ppm; ^1H NMR (300 MHz, $CDCl_3$): δ 2.39 (s, 3H, Me), 6.97 (d, J = 7.8 Hz, 1H), 7.27-7.39 (m, 11H), 7.54 (s, H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 20.97 (s, CH_3), 117.87 (d, J_{CP} = 4.5 Hz, CN), 117.96 (d, J_{CP} = 33.8 Hz, C), 128.80 (d, J_{CP} = 7.5 Hz, 4CH), 129.32 (s, 2CH), 133.50 (s, CH), 133.62 (s, CH), 133.91 (d, J_{CP} = 20.3 Hz, 4CH), 134.21 (d, J_{CP} = 4.5 Hz, CH), 135.07 (d, J_{CP} = 10.5 Hz, 2C), 139.25 (d, J_{CP} = 18.0 Hz, C), 139.48 (s. C). HRMS: m/z calcd for $C_{20}H_{17}NP$ $[M+H]^+$: 302.1099; found : 302.1101.

*Phosphine **4c***

White solid, 5.05 g, 53 % yield. ^{31}P NMR (121 MHz, $CDCl_3$): δ-7.9 ppm; ^1H NMR (300 MHz, $CDCl_3$): δ 3.69 (s, 3H, MeO), 6.52 (t, J = 3.0 Hz, 1H), 6.90 (dd, J = 2.4, 8.4 Hz, 1H), 7.27-7.41 (m, 10H), 7.66 (dd, J = 3.3, 8.7 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 55.4 (s, CH_3O), 109.3 (d, J_{CP} = 31.5 Hz, C), 113.9 (s, CH), 118.03 (d, J_{CP} = 3.8 Hz, CN), 119.7 (s, CH), 128.9 (d, J_{CP} = 7.5 Hz, 4CH), 129.5 (s, 2CH), 134.1 (d, J_{CP} = 20.3 Hz, 4CH), 134.5 (d, J_{CP} = 10.5 Hz, 2C), 135.6 (d, J_{CP} = 5.3 Hz, CH), 145.2 (d, J_{CP} = 20.3 Hz, C), 162.4 (s. C). HRMS: m/z calcd for $C_{20}H_{17}NOP$ $[M+H]^+$: 318.1048; found : 318.1049.

*Procedure B for the Synthesis of 1,2-Azaphosphindoledisulfide **8a**:*

To a solution of **4a** (3 mmol) in THF (20 mL) was added 5 equivalents of lithium wire under N_2 atmosphere. The reaction mixture was stirred for 4 h at room temperature and ^{31}P NMR signal indicated the reaction was complete, then the excess of lithium wire was removed. Then S_8 was added, the reaction mixture was stirred for another 1 h at room temperature. After removal of the solvent under reduced pressure, the residue was treated with water (10 mL), and extracted with dichloromethane. The organic layer was dried over anhydrous Na_2SO_4. After filtration and removal of the solvent, the residue was chromatographed on silica gel (petroleum ether/ethyl acetate).

*1,2-azaphosphindoledisulfide **8a***

Red solid, 372 mg, 45 % yield. ^{31}P NMR (121 MHz, DMSO): δ 95.8 ppm; ^1H NMR (300 MHz, DMSO): δ 3.16 (br s, 1H, NH), 7.70-7.76 (m, 3H), 7.82-8.00 (m, 6H); ^{13}C NMR (75 MHz, DMSO): δ 126.41 (d, J_{CP} = 13.5 Hz, CH), 127.77 (d, J_{CP} = 5.3 Hz, C), 128.29 (d, J_{CP} = 15.8 Hz, C), 129.91 (d, J_{CP} = 10.5 Hz, CH), 129.98 (s, 2CH), 130.68 (s, 2CH), 131.39 (d, J_{CP} =1.5 Hz, CH), 134.81 (s, CH), 137.05 (d, J_{CP} = 12.8 Hz, CH), 147.73 (d, J_{CP} =96.8 Hz, C), 169.83 (d, J_{CP} = 2.3 Hz, C). HRMS: m/z calcd for $C_{13}H_{11}NPS_2$ $[M+H]^+$: 276.0071; found: 276.0072.

*Procedure C for the Synthesis of 2H-1,2-Azaphosphindoles **9-11**:*

To a solution of **4a-4c** (3 mmol) in THF (20 mL) was added 5 equivalents of lithium wire under N_2 atmosphere. The reaction mixture was stirred for 4 h at room temperature and ^{31}P NMR signal indicated the reaction was complete, then the excess of lithium wire was removed. At 0°C, $AlCl_3$ (134 mg, 1 mmol) was added to the reaction mixture. After stirring for an hour at room temperature, R'X (3 mmol benzyl bromide or 1-bromopropane, 1.5 mmol 1, 2-dibromoethane) was added. The reaction mixture was stirred for 12 h and ^{31}P NMR indicated the reaction was complete. Then S_8 was added, the reaction mixture was stirred for another 3 h at 50 °C. After removal of the solvent under reduced pressure, the residue was treated with water (10 mL), and extracted with dichloromethane. The organic layer was dried over anhydrous Na_2SO_4. After filtration and removal of the solvent, the residue was chromatographed on silica gel (petroleum ether/ethyl acetate).

*2H-1,2-azaphosphindole **9a***

Yellow solid, 334 mg, 39 % yield. ^{31}P NMR (121 MHz, $CDCl_3$): δ 89.8 ppm; ^1H NMR (300 MHz, $CDCl_3$): δ 0.95 (dt, J = 0.9, 7.2 Hz, 3H), 1.51-1.67 (m, 2H), 2.09-2.26 (m, 2H), 7.48-7.66 (m, 5H), 7.82-7.95 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 15.17 (d, J_{CP} =16.5 Hz, CH_3), 16.59 (d, J_{CP} =3.8 Hz, CH_2), 35.87 (d, J_{CP} =60.8 Hz, CH_2), 126.44 (d, J_{CP} =13.5 Hz, CH), 128.68 (d, J_{CP} =9.8 Hz, CH), 128.81 (s, 2CH), 129.05 (s, 2CH), 131.74 (d, J_{CP} =9.8 Hz, CH), 131.91 (s, CH), 132.23 (d, J_{CP} =2.3 Hz, CH), 134.38 (d, J_{CP} =22.5 Hz, C), 139.53 (d, J_{CP} =33.8 Hz, C), 142.41 (d, J_{CP} =72.8 Hz, C), 179.10 (d, J_{CP} =6.8 Hz, C). HRMS: m/z calcd for $C_{16}H_{17}NPS$ $[M+H]^+$: 286.0819; found: 286.0818. Anal. Calcd for $C_{16}H_{16}NPS$: C 67.35, H 5.65, N 4.91; found: C 67.56, H 5.35, N 4.87.

2H-1,2-azaphosphindole ***9b***

Yellow solid, 503 mg, 56 % yield. ^{31}P NMR (121 MHz, $CDCl_3$): δ 89.4 ppm; ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.97 (t, *J* = 7.2 Hz, 3H), 1.54-1.65 (m, 2H), 2.14-2.25 (m, 2H), 2.46 (s, 3H), 7.46 (dd, *J* = 3.9, 7.5 Hz, 1H), 7.52-7.63 (m, 4H), 7.80-7.91 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 15.16 (d, J_{CP} = 16.5 Hz, CH_3), 16.63 (d, J_{CP} = 3.8 Hz, CH_2), 21.82(d, J_{CP} = 1.5 Hz, CH_3), 36.04 (d, J_{CP} = 61.5 Hz, CH_2), 127.02 (d, J_{CP} = 12.8 Hz, CH), 128.52 (d, J_{CP} =10.5 Hz, CH), 128.79 (s, 2CH), 129.04 (s, 2CH), 131.78 (s, CH), 132.53 (d, J_{CP} = 9.8 Hz, CH), 134.53 (d, J_{CP} = 23.3 Hz, C), 139.22 (d, J_{CP} = 75.8 Hz, C), 140.15 (d, J_{CP} = 33.8 Hz, C), 143.00 (d, J_{CP} = 2.3 Hz, C), 179.25 (d, J_{CP} = 6.8 Hz, C). HRMS: m/z calcd for $C_{17}H_{19}NPS$ $[M+H]^+$: 300.0976; found: 300.0974.

2H-1,2-azaphosphindole ***10a***

Yellow solid, 280 mg, 28 % yield. ^{31}P NMR (121 MHz, $CDCl_3$): δ 86.4 ppm; ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.74 (d, J_{PH} = 15.0 Hz, 2H), 6.89-6.92 (m, 2H), 7.03-7.10 (m, 3H), 7.48-7.62 (m, 6H), 7.68-7.70 (m, 2H), 7.78-7.83 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 42.63 (d, J_{CP} =55.5 Hz, CH_2), 126.02 (d, J_{CP} =13.5 Hz, CH), 127.11 (d, J_{CP} =4.5 Hz, CH), 128.01 (d, J_{CP} =3.0 Hz, 2CH), 128.70 (s, 2CH), 128.86 (s, 2CH), 129.00 (d, J_{CP} =9.8 Hz, CH), 130.00 (d, J_{CP} =5.3 Hz, 2CH), 130.60 (d, J_{CP} =9.0 Hz, C), 131.49 (d, J_{CP} =9.8 Hz, CH), 131.79 (s, CH), 132.15 (d, J_{CP} =2.3 Hz, CH), 134.21 (d, J_{CP} =23.3 Hz, C), 140.05 (d, J_{CP} =33.8 Hz, C), 140.90 (d, J_{CP} =75.0 Hz, C), 179.85 (d, J_{CP} =7.5 Hz, C). HRMS: m/z calcd for $C_{20}H_{17}NPS$ $[M+H]^+$: 334.0819; found: 334.0819.

2H-1,2-azaphosphindole ***10b***

Yellow solid, 281 mg, 27 % yield. ^{31}P NMR (121 MHz, $CDCl_3$): δ 85.9 ppm; ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.39 (s, 3H, Me), 3.74 (d, J_{PH} = 14.7 Hz, 2H, CH_2), 6.91-6.93 (d, 2H), 7.07-7.09 (d, 3H), 7.37-7.42 (m, 2H), 7.48-7.59 (m, 3H), 7.64-7.69 (t, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 21.82 (s, CH_3), 42.70 (d, J_{CP} = 55.5 Hz, CH_2), 126.64 (d, J_{CP} = 13.5 Hz, CH), 127.08 (d, J_{CP} = 4.5 Hz, CH), 128.01 (d, J_{CP} = 3.8 Hz, 2CH), 128.69 (s, 2CH), 128.84 (2CH), 128.84 (d, J_{CP} = 9.8 Hz, CH), 130.02 (d, J_{CP} = 6.0 Hz, 2CH), 130.74 (d, J_{CP} = 8.3 Hz, C), 131.68 (s, CH), 132.36 (d, J_{CP} = 9.8 Hz, CH), 134.33 (d, J_{CP} = 23.3 Hz, C), 137.69 (d, J_{CP} = 78.0 Hz, C), 140.58 (d, J_{CP} = 33.8 Hz, C), 143.01 (d, J_{CP} = 2.3 Hz, C), 179.94 (d, J_{CP} = 6.8 Hz, C). HRMS: m/z calcd for $C_{21}H_{19}NPS$ $[M+H]^+$: 348.0976; found: 348.0975. Anal. Calcd for $C_{21}H_{18}NPS$: C 72.60, H 5.22, N 4.03; found: C 72.56, H 5.45, N 3.87.

2H-1,2-azaphosphindole ***10c***

Yellow solid, 404 mg, 37 % yield. ^{31}P NMR (121 MHz, $CDCl_3$): δ 84.7 ppm; ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.69 (m, 2H, CH_2), 3.84 (s, 3H, OMe), 6.94-6.99 (m, 3H), 7.05-7.12 (m, 3H), 7.21 (dd, *J* = 2.4, 9.3 Hz, 1H), 7.45-7.57 (m, 4H), 7.66-7.69 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 42.64 (d, J_{CP} = 55.5 Hz, CH_2), 56.06 (s, OMe), 113.85 (d, J_{CP} = 10.5 Hz, CH), 118.15 (d, J_{CP} = 1.5 Hz, CH), 127.15 (d, J_{CP} = 3.8 Hz, CH), 127.45 (d, J_{CP} = 15.8 Hz, CH), 128.02 (d, J_{CP} = 3.8 Hz, 2CH), 128.64 (s, 2CH), 128.82 (s, 2CH), 130.05 (d, J_{CP} = 6.0 Hz, 2CH), 130.65 (d, J_{CP} = 9.0 Hz, C), 131.67 (s, CH), 133.03 (d, J_{CP} = 33.8 Hz, C), 134.44 (d, J_{CP} = 24.0 Hz, C), 143.95 (d, J_{CP} = 74.3 Hz, C), 162.59 (d, J_{CP} = 12.8 Hz, C), 179.58 (d, J_{CP} = 7.5 Hz, C). HRMS: m/z calcd for $C_{21}H_{19}NOPS$ $[M+H]^+$: 364.0925; found: 364.0923.

2H-1,2-azaphosphindoles ***11a*** *and* ***11a'***

a yellow solid containing an inseparable mixture of two diastereoisomers, 479 mg, 62 % yield. ^{31}P NMR (121 MHz, $CDCl_3$): δ 88.01 (s, minor isomer) and 87.88 (s, major isomer) ppm; ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.45-2.61 (m, 4H), 7.49-7.67 (m, 10H), 7.85-7.98 (m, 8H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 27.61 (m, CH_2, mixture of two isomers), 126.82 (m, CH, mixture of two isomers), 128.87(s, CH, minor isomer), 128.92(s, CH, major isomer), 129.01(s, CH, mixture of two isomers), 129.17(s, CH, minor isomer), 129.22(s, CH, major isomer), 132.11 (t, *J* =4.5 Hz, CH, mixture of two isomers), 132.25 (d, *J*=2.3 Hz, CH, mixture of two isomers), 132.74 (s, CH, mixture of two isomers), 134.06 (td, *J* =3.8, 11.3 Hz, C, mixture of two isomers), 139.62 (t, *J* =17.3 Hz, C, mixture of two isomers), 141.21 (td, *J* =9.8, 38.3 Hz, C, mixture of two isomers), 180.12 (m, C=N, mixture of two isomers). HRMS: m/z calcd for $C_{26}H_{23}N_2P_2S_2$ $[M+H]^+$: 513.0778; found: 513.0780. Anal. Calcd for $C_{28}H_{22}N_2P_2S_2$: C 65.61, H 4.33, N 5.47; found: C 65.36, H 4.65, N 5.27.

2H-1,2-azaphosphindoles ***11b*** *and* ***11b'***

a yellow solid containing an inseparable mixture of two diastereoisomers, 487 mg, 60 % yield. ^{31}P NMR (121 MHz, $CDCl_3$): δ 87.65 (s, minor isomer) and 87.47 (s, major isomer) ppm; ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.34-2.53 (m, 10H), 7.46-7.67 (m, 10H), 7.78-7.94 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 21.86 (s, CH_3, mixture of two isomers), 27.80 (td, *J* =3.8, 27.8 Hz, CH_2, mixture of two isomers), 127.36 (dd, *J* =6.8, 12.0 Hz, CH, mixture of two isomers), 128.73 (d, *J* =4.5 Hz, C, mixture of two isomers), 128.82(s, C, minor isomer), 128.87(s, C, major isomer), 129.13(s, C, minor isomer), 129.18(s, C, major isomer),

132.03(s, CH, minor isomers), 132.08(s, CH, major isomers), 132.88 (dd, *J* =4.5, 9.0 Hz, CH, , mixture of two isomers), 134.23 (td, *J*=4.5, 12.0 Hz, C, , mixture of two isomers), 137.96(td, *J* =8.3, 39.0 Hz, C, mixture of two isomers), 140.24 (t, *J* =17.8 Hz, C, , mixture of two isomers), 143.65 (s, C, mixture of two isomers), 180.23 (t, *J* = 3.0 Hz, C=N, mixture of two isomers). HRMS: m/z calcd for $C_{30}H_{27}N_2P_2S_2$ $[M+H]^+$: 541.1091; found: 541.1096.

*Procedure D for the Synthesis of Compound **14**:*

To a solution of **4b** (3 mmol) in THF (20 mL) was added 5 equivalents of lithium wire under N_2 atmosphere. The reaction mixture was stirred for 4 h at room temperature and ^{31}P NMR signal indicated the reaction was complete, then the excess of lithium wire was removed and degassed H_2O (6 mmol, 108 mg) was added. The reaction mixture was stirred for 10 min at room temperature. After removal of the solvent under reduced pressure, dichloromethane was added to the reaction mixture while stirring. After 10 min, N-phenylmaleimide (3 mmol, 520 mg) was added to the reaction mixture at room temperature. Then S_8 (3.3 mmol, 106 mg) was added after 2h. The reaction mixture was stirred for another 2 h at 30 °C. The organic layer was dried over anhydrous Na_2SO_4. After filtration and removal of the solvent, the residue was chromatographed on silica gel (petroleum ether/ethyl acetate).

*Compound **14***

Light yellow solid, 646 mg, 50 % yield. ^{31}P NMR (121 MHz, DMSO): δ 65.0 ppm; ^1H NMR (300 MHz, DMSO): δ 2.26 (s, 3H, Me), 4.10 (dd, *J* =9.0, 15.3 Hz, 1H), 4.57 (dd, *J* =4.5, 8.7 Hz, 1H), 6.30 (d, *J* =2.1 Hz, 1H, NH), 6.36-6.39 (m, 2H), 6.52 (s, 1H), 7.31-7.39 (m, 4H), 7.46-7.62 (m, 4H), 7.93 (d, *J* =6.9 Hz, 2H); ^{13}C NMR (75 MHz, DMSO): 21.68(s, Me), 51.12 (d, *J* =43.5 Hz, CH), 54.90 (s, CH), 70.41(d, *J* =12.0 Hz, C), 123.78(d, *J* =9.8 Hz, CH), 126.42(d, *J* =9.8 Hz, CH), 126.88(s, 2CH), 128.88(s, 2CH), 129.03(s, 2CH), 129.24(d, *J* =96.0 Hz, C), 129.28(s, 4CH), 130.09(d, *J* =12.8 Hz, CH), 131.83(s, C), 138.11(d, *J* =14.3 Hz, C), 143.16(d, *J* =2.3 Hz, C), 149.37(d, *J* =11.3 Hz, C), 170.54(d, *J* =3.0 Hz, C), 173.29(d, *J* =5.3 Hz, C). HRMS: m/z calcd for $C_{24}H_{20}N_2O_2PS$ $[M+H]^+$: 431.0983; found: 431.0985.

Supplementary information available:

X-ray data for **8a**: CCDC no **1430795** and **14**: CCDC no **1533720**.

Acknowledgements

This work was supported by the National Natural Science Foundation (21672193, 21272218) and Zhengzhou University of China.

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