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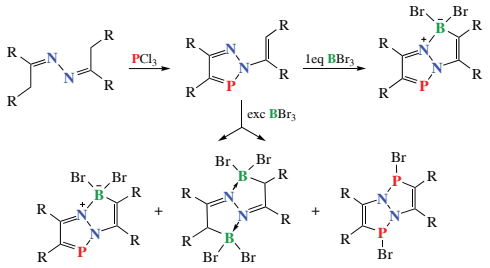
Synthesis of 3a,6a-diaza-1-phospha-4-borapentalenes based on ketazines

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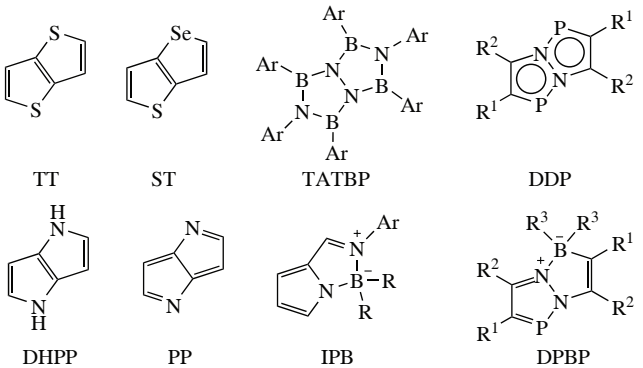
A two-step synthesis for heteropentalenes with phosphorus, boron, and nitrogen as heteroatoms involves ketazine treatment with PCl_3 to form diazaphosphole followed by the reaction with BBr_3 yielding 4,4-dibromo-3a,6a-diaza-1-phospha-4-bora-pentalene. Minor symmetrization products, bromine-substituted 3a,6a-diaza-1,4-diborapentalene and 3a,6a-diaza-1,4-diphosphapentalene, were also isolated. These compounds can serve as precursors for luminescent materials *via* bromine replacement.



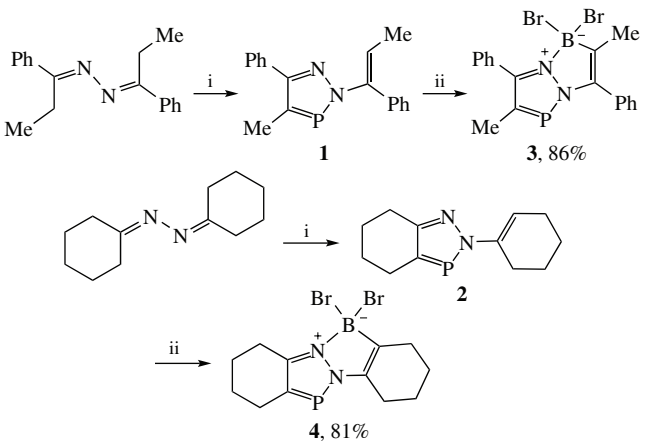
Keywords: diazaphosphole, ketazine, heteropentalenes, boron tribromide, diazadiphosphapentalene, organoboron compounds, organophosphorus compounds.

Over the last two decades, a remarkable growth in applied research on heteroatom-containing pentalenes (heteropentalenes) has been noted, with the objective of employing them as active parts in organic light-emitting diodes and organic field-effect transistors.[1] Among the numerous potential combinations of various heteroatoms, the derivatives of thieno[3,2-*b*]thiophenes (TTs) and 1,4-dihydropyrrolo[3,2-*b*]pyrroles (DHPPs) have been the most extensively studied ones, along with stable heteropentalenes (PPs) that exhibit antiaromaticity.[2,3] Such compounds have a narrow HOMO–LUMO energy gap and a low barrier between the singlet and triplet states, which is important for applications in organic electronics. Heteropentalenes containing boron atoms (IPB, TATBP) exhibit unique optoelectronic characteristics, in particular phosphorescence.[4,5]

Diazadiphosphapentalenes (DDPs) that we are currently developing may be considered the least studied class of heteropentalenes. Nonetheless, it has been shown that the charge transfer complexes derived from them possess photoconductive properties,[6,7] while the DDPs themselves tend to form multilayer structures, with their optoelectronic characteristics being modulated by the spacing between the layers.[8,9] Thus, it is apparent that creating new varieties of heteropentalenes is an important task. This paper discusses the synthesis of 3a,6a-diaza-1-phospha-4-borapentalenes (DPBPs) containing phosphorus and boron atoms in the pentalene framework.



Previously, we discovered that during the synthesis of DDPs from ketazines, in a number of cases diazaphospholes were formed as by-products, which were, in fact, intermediates of this reaction.[10] Herein, using strictly equimolar amounts of ketazine and phosphorus trichloride, as well as a reduced temperature (–10 °C), we were able to isolate the previously described diazaphospholes **1** and **2** in yields of about 90% (Scheme 1). As it turned out, diazaphospholes **1** and **2** readily reacted with boron tribromide in toluene to form 3a,6a-diaza-1-phospha-4-borapentalenes **3** and **4**, respectively, as the main products in yields of about 80%. These compounds crystallized from the reaction mixture within an hour. A convenient circumstance is that these reactions do not require a hydrogen bromide acceptor. The molecular structures of compounds **3**



Scheme 1 *Reagents and conditions*: i, PCl_3, MeCN, 0 °C; ii, BBr_3, PhMe, 0 °C, 1 h.

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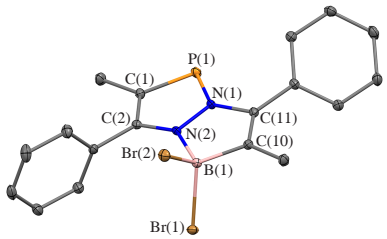


Figure 1 Molecular structure of DPBP **3**. Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms are omitted.

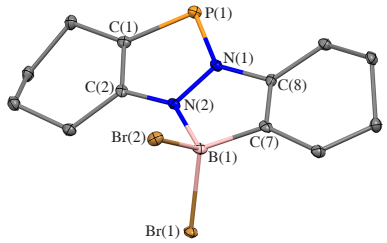


Figure 2 Molecular structure of DPBP **4**. Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms are omitted.

and **4** were determined by single-crystal X-ray diffraction studies (Figures 1 and 2).†

† *Crystal data for* **3**. $C_{18}H_{16}BBr_2N_2P$ (M = 461.93), triclinic, space group $P\bar{1}$, a = 9.5215(4), b = 9.8843(4) and c = 11.0772(4) Å, α = 75.323(4), β = 70.957(3) and γ = 74.092(4)°, V = 932.18(7) Å^3, Z = 2, d_{calc} = 1.646 g cm^{-3}, μ = 4.435 mm^{-1}, F_{000} = 456. A yellow prism-shaped single crystal with dimensions of 0.31×0.28×0.22 mm was selected, and the intensities of 19186 reflections were measured using a Tongda TD-5000 diffractometer (ω-scans technique, λ[MoK_α] = 0.71073 Å, $2\theta_{max}$ = 52.044°). After merging of equivalents and absorption corrections, 3601 independent reflections (R_{int} = 0.0425) were used for the structure solution and refinement. Final R factors: R_1 = 0.0249 [3325 reflections with $I > 2\sigma(I)$], wR_2 = 0.0646 (all reflections), GOF = 1.039. Largest diff. peak and hole 0.525 and –0.426 e Å^{-3}.

Crystal data for **4**. $C_{12}H_{16}BBr_2N_2P$ (M = 389.87), orthorhombic, space group *Pbca*, a = 13.6331(7), b = 13.2291(7) and c = 15.7273(11) Å, V = 2836.5(3) Å^3, Z = 8, d_{calc} = 1.826 g cm^{-3}, μ = 5.811 mm^{-1}, F_{000} = 1536. A yellow prism-shaped single crystal with dimensions of 0.28×0.25×0.18 mm was selected, and the intensities of 73414 reflections were measured using a Tongda TD-5000 diffractometer ($2\theta_{max}$ = 60.066°). After merging of equivalents and absorption corrections, 4139 independent reflections (R_{int} = 0.1345) were used for the structure solution and refinement. Final R factors: R_1 = 0.0469 [3401 reflections with $I > 2\sigma(I)$], wR_2 = 0.1095 (all reflections), GOF = 1.076. Largest diff. peak and hole 1.740 and –0.678 e Å^{-3}.

Crystal data for **5**. $C_{18}H_{18}B_2Br_4N_2{\cdot}0.5(CH_2Cl_2)$ (M = 646.07), monoclinic, space group C_2/c, a = 22.3087(9), b = 15.1831(4) and c = 13.5579(5) Å, β = 101.843(4)°, V = 4494.5(3) Å^3, Z = 8, d_{calc} = 1.910 g cm^{-3}, μ = 7.290 mm^{-1}, F_{000} = 2488. A yellow prism-shaped single crystal with dimensions of 0.24×0.21×0.19 mm was selected, and the intensities of 101856 reflections were measured using a Tongda TD-5000 diffractometer ($2\theta_{max}$ = 30.066°). After merging of equivalents and absorption corrections, 6571 independent reflections (R_{int} = 0.1002) were used for the structure solution and refinement. Final R factors: R_1 = 0.0295 [5841 reflections with $I > 2\sigma(I)$], wR_2 = 0.0698 (all reflections), GOF = 1.119. Largest diff. peak and hole 0.923 and –0.744 e Å^{-3}.

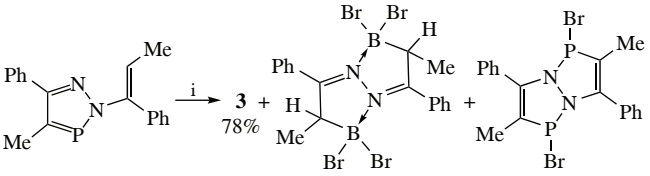
To analyze the obtained data (indexing, data integration, frame scaling and absorption correction), we used the CrysAlisPro software package.[13] The structures were solved by dual method[14] and were refined on F^2_{hkl} using SHELXL program.[15] All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were placed in calculated positions and were refined in the riding model [U_{iso}(H) = 1.5 U_{eq}(C) for CH_3-group and U_{iso}(H) = 1.2 U_{eq}(C) for other groups].

CCDC 2561083–2561085 contain the supplementary crystallographic data for this parer. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* https://www.ccdc.cam.ac.uk.

In both compounds, the boron centers are tetracoordinate and adopt almost ideal tetrahedral geometry[11,12] ($\tau4'$ = 0.96 and 0.92 for **3** and **4**, respectively). The heteropentalene frameworks in compounds **3** and **4** are nearly planar, with an average deviation of atoms from the mean planes of 0.034 and 0.013 Å, respectively. The largest deviations are observed for boron atoms (0.063 Å for compound **3** and 0.029 Å for compound **4**). Bond lengths in the heteropentalene frameworks of compounds **3** and **4** are relatively similar. The B(1)–N(2) coordination bonds in compounds **3** and **4** are 1.563(3) and 1.572(5) Å, as are those in five-membered chelate boron-containing rings.[5] The carbon–carbon bonds in the heteropentalene framework of each DPBP are not equivalent. The C–C bond lengths of the diazaphosphole rings [1.392(3) Å in **3**, 1.388(5) Å in **4**] are characteristic of aromatic bonds, while those of the boron-containing rings [1.344(3), 1.329(5) Å] fall within the range typical of olefinic C=C bonds. The geometry of the heteropentalene framework is largely unaffected by the peripheral environment. The dihedral angles between the phenyl and DPBP planes in **3** are 82.3 and 41.8° for substituents at C(2) and C(11) atoms, respectively. The structure of the cyclohexene fragments in **4** is determined by the presence of double and aromatic bonds and, accordingly, by the small torsion CCCC angles at them (2.6 and 1.1°). Within the crystal lattice, molecules of complex **3** form dimeric pairs through intermolecular Br···P contacts (see Online Supplementary Materials, Figure S1). In contrast, molecules of complex **4** self-assemble into one-dimensional molecular chains *via* Br···H hydrogen bonding interactions (Figure S2).

3a,6a-Diaza-1-phospha-4-borapentalenes **3** and **4** were characterized by ^{1}H, ^{31}P, ^{13}C, ^{11}B NMR spectroscopy. Both compounds manifest singlets in the ^{31}P{^{1}H} spectra at 199.7 and 189.9 ppm, respectively, in the downfield region characteristic of azaphospholes. In the ^{11}B NMR spectra of these compounds, singlets at δ –3.11 and –3.98 ppm appear, confirming the formation of tetracoordinate boron moiety.

When carrying out reactions of diazaphospholes **1**, **2** with excess boron tribromide, we found that the mother liquor after separation of the corresponding zwitterionic dibromides (**3**, **4**) contained minor products with better solubility. We were able to isolate and fully characterize the by-products of the reaction between diazaphosphole **1** and BBr_3, which were in fact the symmetrization products (Scheme 2). One of the products, tetrabromo diazadiborapentalene **5**, was a colorless crystalline powder. Its single crystals of **5** suitable for X-ray diffraction were grown from dichloromethane (Figure 3).†



1 **5**, 10% **6**, 9%

Scheme 2 *Reagents and conditions*: i, BBr_3 (2 equiv.), PhMe, 0 °C.

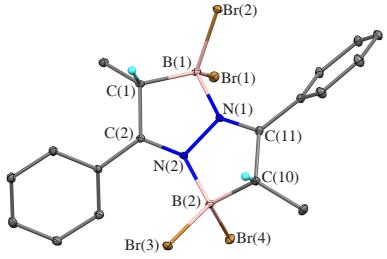


Figure 3 Molecular structure of compound **5**. Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms of Ph and Me groups are omitted.

Five-membered heterocycles in compound **5** have an sp^3 hybridized carbon atom, which causes the heteropentalene framework to be non-planar. This distinguishes compound **5** from the known tetrahalogen-substituted diborapentalenes with a flat framework.[16] The lengths of the N–B coordination bonds are close to those of DPBPs **3** and **4**. The shortened N–C bond distances [1.303(3) and 1.312(3) Å] unambiguously indicate a double-bond character in compound **5**. In turn, the C–C bonds correspond to sp^3–sp^2 single carbon–carbon bonds. In solution, however, molecule **5** is represented by several isomers, as can be seen from the ^{1}H NMR spectrum, showing the nonequivalence of the methyl groups and nearby protons of the framework (see Online Supplementary Materials). In the ^{11}B NMR spectrum of compound **5**, a singlet is observed at –1.15 ppm, located in the same region as for 3a,6a-diaza-1-phospha-4-borapentalenes **3** and **4**.

The second minor product of the reaction between **1** and BBr_3 was dibromo diazadiphosphapentalene **6**, which was isolated as orange crystals. Its ^{31}P{^{1}H} NMR spectrum contains a characteristic broadened signal at 128 ppm typical of dibromo derivatives of diazadiphosphapentalenes.[17] In the ^{1}H NMR spectrum, signals for phenyl and methyl groups are observed.

Since dibromine-substituted heteropentalenes **3** and **4** are thermally very stable and do not undergo symmetrization upon heating, we believe that the formation of by-products in the reactions of diazaphospholes **1** and **2** with BBr_3 is due to the presence of HBr in the reaction mixtures, which can cause cleavage of the diazaphosphole ring with the formation of ketazine and PBr_3.

To conclude, we have developed a synthetic approach to 3a,6a-diaza-1-phospha-4-borapentalenes, new heterocycles containing boron and phosphorus atoms in the heteropentalene framework. A detailed study showed that during the synthesis small amounts of easily separable symmetrization minor products, 1,1,4,4-tetrabromo-1,4-diborapentalenes and 1,4-dibromo-3a,6a-diaza-1,4-diphosphapentalenes, were formed.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.71267/mencom.8125.

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