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Phosphorus Heterocycles

Photoisomerizable Heterodienes Derived from a Phosphine Borane[**]

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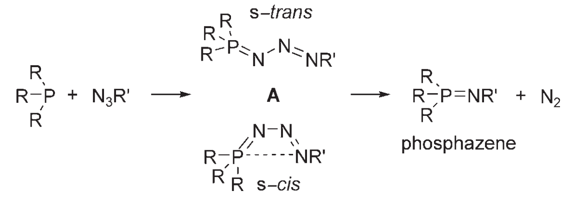
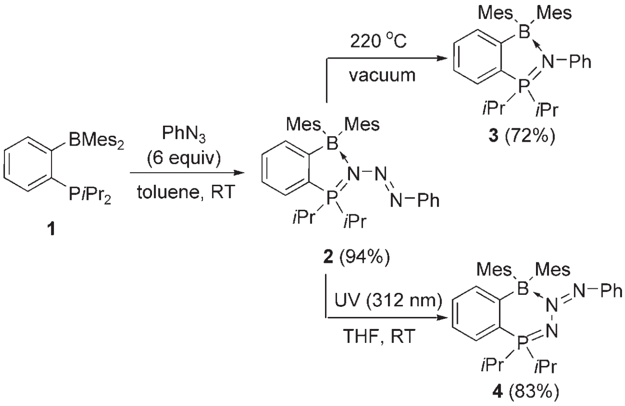
The coupling of tertiary phosphines and azides, commonly referred to as the Staudinger reaction (Scheme 1), provides a straightforward route to phosphazenes.[1] Numerous applications of this reaction have been made in organic synthesis (for the preparation of C=N bonds, in conjunction with the aza-Wittig reaction) as well as in chemical biology (for the chemoselective ligation of biologically relevant moieties).[2] Considerable effort has also been devoted to detecting phosphazide intermediates **A**. Accordingly, substituent effects, ring strain, and/or coordination to transition metals were eventually found to impart sufficient stabilization on phosphazides to permit their structural characterization.[3,4] More recently, computational studies have provided more insight into the whole process.[5] In particular, combined experimental and theoretical studies by Grützmacher and coworkers suggested that phosphazides can be significantly stabilized when the nitrogen atom in the α position to the phosphorus is coordinated intramolecularly to a Lewis acid.[5b] This prompted us to investigate the reaction of azides with phosphine borane derivatives *ortho*-$(R_2P)C_6H_4$-(BR'_2) that we have recently introduced as ambiphilic ligands for transition metals.[6] Here we report that the resulting phosphazide has high thermal stability, which allows the study of its photochemical properties. Accordingly, such heterodienes were found to undergo an unprecedented photoisomerization process associated with a change from an $N_\alpha \rightarrow B$ to an $N_\beta \rightarrow B$ interaction. The generality and possible reversibility of these phenomena are demonstrated with a related phosphazine adduct.



Scheme 1. The Staudinger reaction.

The phosphine borane derivative **1**[7] reacted cleanly with phenylazide, although a large excess of PhN_3 was necessary to achieve complete conversion in a reasonable time at room temperature (Scheme 2). The ^{31}P NMR signal for the resulting product **2** ($\delta = +60.6$ ppm) appears at significantly lower field compared to that of **1** ($\delta = +5.5$ ppm), which unambiguously shows the oxidation of the phosphorus atom. The large shift of the ^{11}B NMR signal (from $\delta = +75.0$ ppm in **1** to $\delta = +2.1$ ppm in **2**) indicates a change from a tricoordinate to a tetracoordinate boron atom, and mass spectrometry demonstrates the retention of the three nitrogen atoms. All the spectroscopic data for **2**[7] support a phosphazide structure, whose precise nature was deduced from X-ray analysis (Figure 1a).[8] The nitrogen in the α position to the phosphorus atom strongly interacts with the boron center as indicated by the short N_α–B bond (1.65 Å) and the noticeable pyramidalization of the boron environment (340.7°).[9] This $N_\alpha \rightarrow B$ interaction results in an almost planar five-membered ring. Notably, the heterodiene system of **2** adopts an s-*cis* conformation with a terminal N=N bond of *E* configuration.



Scheme 2. Synthesis, thermal decomposition and photoisomerization of the phosphazide **2**. Mes = mesityl = 2,4,6-trimethylphenyl.

Phosphazide **2** was then subjected to thermal decomposition. Only 10% conversion was reached after heating for 18 h in toluene at reflux, and no decomposition of **2** was observed in the solid state under vacuum until the melting point was reached at around 220 °C. At this stage a rapid but clean loss of nitrogen occurred to give the corresponding phosphazene **3** in 72% yield. The ^{31}P and ^{11}B NMR data for **3** are rather similar to those of **2**. The X-ray analysis of **3**[10] revealed the retention of the N→B interaction.

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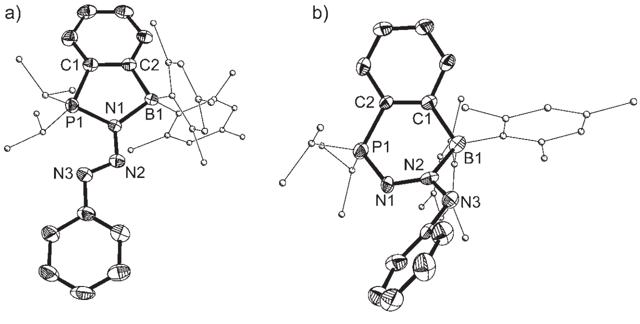


Figure 1. Molecular views (thermal ellipsoids set at 50% probability) of a) **2** and b) **4** in the solid state. Hydrogen atoms are omitted for clarity.

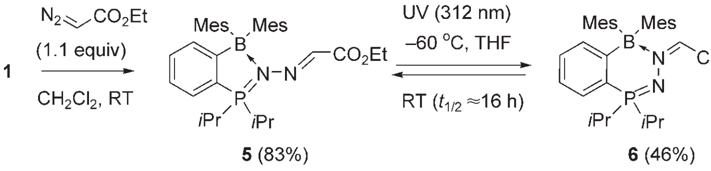
The rather harsh thermal conditions required for the loss of dinitrogen prompted us to investigate the photochemical behavior of **2** as an alternative. Although UV irradiation is a standard method for activating azides and diazo compounds, to the best of our knowledge, this method has not been reported so far with phosphazides as substrates. Irradiation of a solution of **2** in THF at room temperature for four hours ($\lambda = 312$ nm) led to the establishment of a photostationary equilibrium which consisted of about 15% of **2** and 85% of a new product with a ^{31}P NMR signal ($\delta = +34.7$ ppm) that is markedly different from that of the related phosphazene **3**. The new compound was isolated by precipitation from pentane. The ^{11}B NMR spectrum ($\delta = +5.4$ ppm) indicates the retention of the tetracoordinate boron center and the mass spectrum showed no loss of dinitrogen, which suggests that an isomerization process had occurred. An X-ray analysis allowed us to assign the structure of the new product as the phosphazide isomer **4** (Figure 1b). Derivative **4** is only the second example of an N_β-coordinated phosphazide.[4b] The isomerization from $N_\alpha \rightarrow B$ to $N_\beta \rightarrow B$ coordination does not noticeably affect the strength of the $N \rightarrow B$ interaction, as deduced from the very similar N–B bond length and boron pyramidalization (Table 1). The six-membered ring which resulted from the $N_\beta \rightarrow B$ interaction strongly deviates from planarity and adopts a flattened-boat conformation. Notably, the isomerization from $N_\alpha \rightarrow B$ to $N_\beta \rightarrow B$ coordination is accompanied by a change of both the phosphazide conformation (from s-*cis* to s-*trans*) and the N=N bond configuration (from *E* to *Z*).[12] Although the interconversion between *E* and *Z* azo compounds is a well-known process, the conversion of **2** into **4** provides the first example of phosphazide isomerization.[10]

Table 1: Selected bond lengths [Å] and angles [°] for compounds **2**–**6**.

Compound	2	3	4	5	6
Σ_αB	340.8(2)	340.1(6)	340.6(2)	339.9(6)	340.2(9)
P=N$_\alpha$	1.687(2)	1.631(2)	1.633(4)	1.663(2)	1.609(3)
N–B	1.649(2)	1.713(4)	1.684(7)	1.690(3)	1.662(4)
P-NN-X (X=N or C)	1.4(2)	–	163.2(3)	−169.2(2)	−162.6(2)

Intrigued by the possible reversibility of the isomerization between **2** and **4**, we next attempted to convert **4** back into **2** under various thermal and photochemical conditions. However, complex mixtures were obtained and only small amounts of the N_α-coordinated phosphazide **2** could be observed.

To demonstrate the generality and eventually the reversibility of the unusual photoisomerization process observed for the phosphazide **2**, the formation and photochemical behavior of a related phosphazine were then investigated. The phosphine borane derivative **1** was treated with ethyl diazoacetate to afford the corresponding adduct **5** in 83% yield (Scheme 3).[7] The ^{31}P and ^{11}B NMR data for **5** (δ ^{31}P = +64.9 ppm and δ ^{11}B = +2.9 ppm) are very similar to those of **2**. The X-ray analysis performed on **5**[8,12] established the presence of the $N_\alpha \rightarrow B$ interaction, the s-*trans* conformation of the heterodiene framework, and the *E* configuration of the C=N bond. As anticipated, the phosphazine **5** was found to have very high thermal stability (no decomposition occurred upon heating **5** under vacuum, even above the melting temperature of the solid). By analogy with the related phosphazide, the phosphazine **5** was found to isomerize readily upon irradiation ($\lambda = 312$ nm) of the solution in THF, and a photostationary equilibrium between the starting material **5** and a new product **6** of around 20:80, respectively, was obtained within 24 h at −60 °C. The ^{31}P NMR chemical shift for **6** ($\delta = +29.9$ ppm) is very similar to that of the N_β-coordinated phosphazide **4**, which suggests that a related isomerization of $N_\alpha \rightarrow B$ to $N_\beta \rightarrow B$ coordination had occurred. This was unambiguously confirmed by low-temperature isolation and X-ray analysis of **6**,[8] which provided the first example of an N_β-coordinated phosphazine.[13] Notably, the isomerization of **5** to **6** affected the configuration of the C=N bond, but not the conformation of the heterodiene. When the stability of **6** was monitored by ^{31}P NMR spectroscopic analysis of the solution in THF at room temperature and in the dark, the spontaneous and quantitative reisomerization of **6** into **5** with first-order kinetics ($t_{1/2} \approx 16$ h) was revealed.[7]



Scheme 3. Synthesis and reversible isomerization of the phosphazine **5**.

In conclusion, the Staudinger reaction between phenylazide and a phosphine borane derivative was shown to give a phosphazide with high thermal stability as a result of an intramolecular $N_\alpha \rightarrow B$ interaction. This heterodiene undergoes an unprecedented photoisomerization process associated with a change from an $N_\alpha \rightarrow B$ to an $N_\beta \rightarrow B$ interaction. The generality and possible reversibility of such behavior have been demonstrated. Indeed, for the related phosphazine adduct obtained from ethyl diazoacetate, the $N_\beta \rightarrow B$ coordination, which was photochemically generated, could be thermally transformed back to the $\mathrm{N}_\alpha\rightarrow\mathrm{B}$ interaction in solution. These results extend the synthetic interest of ambiphilic compounds which have recently led to spectacular achievements not only as bifunctional organocatalysts,[14] but also as molecular probes[15,16] and dihydrogen activators.[17] Accordingly, ambiphilic derivatives may be considered general scaffolds for new photoisomerizable systems,[18] whose physicochemical properties might be finely tuned. With this in mind, further investigations will focus on the structural and electronic factors governing the coordination isomerization of such heterodienes.

Experimental Section

All reactions and manipulations were carried out under an atmosphere of dry argon, using standard Schlenk techniques. All NMR spectra were recorded at 293 K unless otherwise stated.

2: Phenylazide (240 mg) was added to a solution of **1** (150 mg) in toluene (1.5 mL) at room temperature. After 48 h, the solvent and excess azide were removed under vacuum. The resulting solid was washed with pentane to give spectroscopically pure material (180 mg, 94 % yield); m.p. 220–222 °C; $^{31}\mathrm{P}\{^{1}\mathrm{H}\}$ NMR (121.5 MHz, $\mathrm{CDCl_3}$): $\delta = +61.0$ ppm; ^{11}B NMR (96.3 MHz, $\mathrm{CDCl_3}$): $\delta = +2.1$ ppm; EIMS (70 eV): m/z (%): 561 (<1) [M^+], 442 (25) [$M-\mathrm{Mes}$]$^+$.

3: A powdered sample of **2** (50 mg) was heated to melting point under vacuum until no further loss of nitrogen was observed (approximately 5 min). The resulting light yellow solid was washed with pentane and recrystallized from diethyl ether at −18 °C to give **3** as colorless crystals (36 mg, 72 % yield); m.p. 217–219 °C; $^{31}\mathrm{P}\{^{1}\mathrm{H}\}$ NMR (121.5 MHz, $\mathrm{C_6D_6}$): $\delta = +55.8$ ppm; ^{11}B NMR (96.3 MHz, $\mathrm{C_6D_6}$): $\delta = +6.8$ ppm; EIMS (70 eV): m/z (%): 533 (<1) [M^+], 490 (<1) [$M-i\mathrm{Pr}$]$^+$, 414 (100) [$M-\mathrm{Mes}$]$^+$.

4: A solution of **2** (60 mg) in THF was irradiated with a 312 nm UV lamp at room temperature for 4 h. The solution was warmed to room temperature and the solvent was removed under vacuum. The resulting solid was washed with pentane and recrystallized from THF at −18 °C to give colorless crystals (50 mg, 83 % yield): m.p. 208–210 °C; $^{31}\mathrm{P}\{^{1}\mathrm{H}\}$ NMR (121.5 MHz, $\mathrm{CDCl_3}$): $\delta = +34.7$ ppm; ^{11}B NMR (96.3 MHz, $\mathrm{CDCl_3}$): $\delta = +5.4$ ppm; EIMS (70 eV): m/z (%): 561 (<1) [M^+], 442 (25) [$M-\mathrm{Mes}$]$^+$.

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[7] See the Supporting Information for details.

[8] CCDC-631086–631090 contain the supplementary crystallographic data for compounds **2**–**6**, respectively, for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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