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Phosphorus–nitrogen compounds: Synthesis and spectral investigations on new *spiro*-cyclic phosphazene derivatives

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Abstract

The condensation reaction of {*N*-[(2-hydroxyphenylmethyl)amino]-4,6-dimethylpyridine} (**2**), which is a reduction product of **1**, with trimer $N_3P_3Cl_6$ affords partially a substituted *spiro*-cyclic phosphazene derivative (**3**). The fully substituted phosphazenes (**4** and **5**) have also been obtained from the reactions of **3** with the excess of pyrrolidine and morpholine. The characterizations and spectral investigations of these compounds have been made by elemental analyses, FTIR, ^{1}H-, ^{13}C-, ^{31}P NMR, correlation spectroscopy (COSY), heteronuclear chemical shift correlation (HETCOR), heteronuclear multiple-bond correlation (HMBC) and mass spectroscopy (MS). The salient features of spectral data of these compounds have been discussed.

Keywords: Synthesis of phosphazene derivatives; *spiro*-Phosphazenes; Spectroscopic studies of phosphazenes; HETCOR; HMBC

1. Introduction

Cyclophosphazenes are an important family of inorganic ring systems, which traditionally have received attention for two main reasons: (i) to obtain small molecules of phosphazene derivatives [1,2] and (ii) to produce polymeric phosphazene derivatives [3]. They also play an important role in the chemistry of heteroatom compounds. In recent years, phosphazene polymers have attracted considerable attention because they can be tailored to possess a wide variety of physical and chemical properties by changing the side groups [4,5]. The coordination chemistry of the various multi-site ligands derived from cyclophosphazenes is extremely interesting new area. Phosphazenes have been proposed for a broader array of applications including flame-retardants [6,7], rechargeable lithium batteries [8,9], microencapsulant membranes, high performance fluids and ionic conductors [10], the further design of the highly selective anticancer [11], antibacterial [12], anti-HIV [13] and artificial bone [14] agents.

In this study, the novel *spiro*-cyclic phosphazene derivatives (**4**,**5**) have been obtained (Scheme 1) and their spectroscopic characterizations have been carried out. Total assignments of ^{1}H-, ^{13}C- and ^{31}P NMR spectra for the structures were made with help of H–H correlation spectroscopy (H–H COSY), as well as heteronuclear chemical shift correlation (HETCOR) and heteronuclear multiple-bond correlation (HMBC).

2. Experimental

2.1. Reagents and materials

Hexachlorocyclotriphosphazatriene, $N_3P_3Cl_6$, was purchased from Aldrich and recrystallized from dry hexane followed by sublimation twice before use. 2-Hydroxybenzaldehyde, triethylamine (99.5%), aminopyridines and sodium borohydride were purchased from Fluka and used as received. All experimental manipulations were carried out under argon atmosphere. Solvents tetrahydrofuran (98%), dichloromethane (98%), acetonitrile (99.5%) and light petroleum were dried by standard methods prior to use. Melting points were measured on a Gallenkamp apparatus using a capillary tube. ^{1}H-, ^{13}C-, ^{31}P NMR, HETCOR and HMBC spectra were obtained on a Bruker DPX FT NMR (500 MHz) spectrometer ($SiMe_4$ as internal standard and 85% H_3PO_4 as an external standard). Spectrometer equipped with a 5 mm PABBO BB-inverse gradient probe. The concentration of solute molecules was 150 mg in 1.0 mL $CDCl_3$. Standard Bruker pulse

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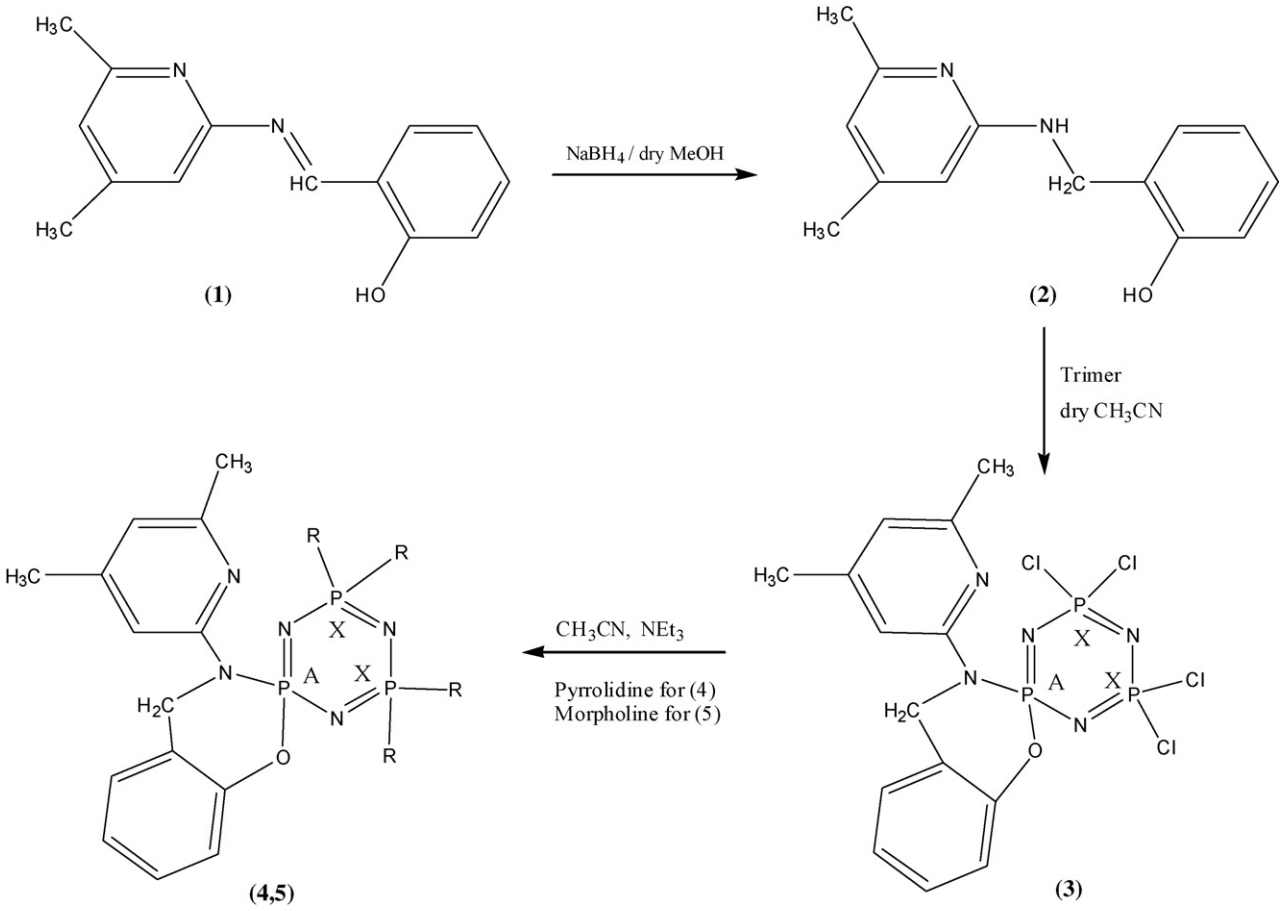

Scheme 1.

programs [15] were used throughout the entire experiment. FTIR spectra were recorded on a Jasco 300E FTIR spectrometer in KBr discs and were reported in cm^{-1} units. Microanalyses were carried out by Medicinal Plants and Medicine Research Center of Anadolu University Eskişehir (Turkey). Electrospray ionization mass spectrometric (ESI-MS) analyses were performed on the AGILEND 1100 MSD spectrometer.

2.2. Synthesis of ligands

Preparation of compounds (**1**–**3**) were carried out as in Scheme 1, adapting a reported procedure [16]. 2-[(1E)-2-aza-2-(4,6-dimethyl(2-pyridyl))vinyl] (**1**) has been obtained using a method in which salicylaldehyde (4.87 g, 3.99 mmol) and 4,6-dimethyl-2-aminopyridines (4.88 g, 3.99 mmol) were refluxed in MeOH (50 mL). The resulting solid was crystallized from MeOH. For the synthesis of *N*-[2-hydroxy(phenylmethyl)amino]-4,6-dimethylpyridine (**2**), 2-[(1E)-2-aza-2-(4,6-dimethyl(2-pyridyl))vinyl] (**1**) (7.64 g, 33.9 mmol) was refluxed in MeOH (50 mL) for 1 h and then equimolar amount of sodium borohydride (1.28 g, 33.9 mmol) was partially added to the reaction mixture. The reduction was completed after 2 h. Then, the solvent was evaporated in reduced pressure, the residue was dissolved in dichloromethane and washed with water. Compound (**2**) was crystallized from MeOH.

2.3. Synthesis of phosphazene derivatives

4,4′,6,6′-Tetrachloro-3,4-dihydro-3-(4,6-dimethylpyridin-2-yl)*spiro*-[1,3,2-benzoxazaphosphinine-2,2′-(2λ^5,4λ^5,6λ^5-cyclotriphosphazene)] (**3**), the synthesis and solid state structure of **3** have been published and it was prepared according to the published procedure [17]. 4,4′,6,6′-Tetrapyrrolidine-3,4-dihydro-3-(4,6-dimethylpyridin-2-yl)*spiro*-[1,3,2-benzoxazaphosphinine-2,2′-(2λ^5,4λ^5,6λ^5-cyclotriphosphazene)] (**4**), 4,4′,6,6′-tetrachloro-3,4-dihydro-3-(4,6-dimethylpyridin-2-yl)*spiro*-[1,3,2-benzoxazaphosphinine-2,2′-(2λ^5, 4λ^5, 6λ^5-cyclotriphosphazene)] (**3**) (2.17 g, 3.38 mmol) and pyrrolidine (1.92 g, 2.24 mL, 27.04 mmol) in acetonitrile (150 mL) were allowed to react by refluxing 62 h. After work-up it was done as in synthesis of compound **3** crystallized from THF/*n*-hexane (2:1), $R_f = 0.57$ [*n*-hexane/THF (2:1)]. 4,4′,6,6′-Tetramorpholine-3,4-dihydro-3-(4,6-dimethylpyridin-2-yl)*spiro*-[1,3,2-benzoxazaphosphinine-2,2′-(2λ^5,4λ^5,6λ^5-cyclotriphosphazene)] (**5**), the work-up procedure of this compound was as in the preparation of **4**. It was recrystallized from THF/light petroleum (bp 40–60) (2:1) $R_f = 0.76$ [THF/*n*-hexane (2:1)]. Experimental and analytical data are listed in Table 1. The ESI-MS spectra of compounds (**1**, **3**–**5**) show the protonated $[M+H]^+$ and deprotonated $[M-H]^+$molecular ion peaks. The elemental analyses results are in agreement with the proposed structures.