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The Synthesis of New Phosphazene-Bearing Ethyl p-Hydroxybenzoate and Ferrocenyl Pendant Groups and their Spectroscopic and Crystallographic Characterizations

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Abstract: This is a study of new hexachlorocyclotriphosphazene ($N_3P_3Cl_6$) derivatives bearing ethyl p-hydroxybenzoate and ferrocenyl pendant groups. Characterizations of the products [mono- **2**, di- (geminal **3a**; non-geminal ***trans*[a]-3b**, ***trans*[b]-3c** and ***cis*-3d**), tri- **4** and tetra- **5** substituted phosphazene derivatives] were performed using elemental analysis and spectral methods. The structures of the two compounds (**2** and **5**) were explained by the use of X-ray diffraction techniques.

Keywords: Ferrocenylphosphazenes, ethyl p-hydroxybenzoate, crystal structure, spectroscopy.

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INTRODUCTION

Halogenocyclophosphazenes are remarkable multi-branched phosphorus–nitrogen compounds used in the synthesis of cyclophosphazene derivatives, from organocyclophosphazenes to dendrimeric cyclophosphazenes. Each phosphorus atom is connected to two exocyclic substituents such as chlorine, fluorine or bromine atoms. The sequential replacement of these halogen atoms in halogenocyclophosphazenes with different reagents can produce new phosphazene derivatives (1, 2). The reactions of $N_3P_3Cl_6$ with bidentate reagents produce different geometrical and optical isomers, e.g., spiro- (mono, di or tri) and bino-structures (3–7). Monospiro products have four reactive P–Cl bonds. The reactions of monospiro cyclophosphazenes with monodentate reagents produce mono-, di- (gem-, nongeminal cis- or nongeminal trans-), tri- and tetra- substituted phosphazene derivatives (8, 9).

Because of their structural features, organocyclophosphazenes are used as polydentate ligands for coordination complexes and multi-branched cores for dendrimers. Recently, organocyclophosphazene-containing coordination complexes have been used as chemosensors for different metals (10–12) and luminescent materials (13). Also, cyclic phosphazene core-based materials are widely

implemented in OLED technology (14–16) and in biomedical applications (17, 18).

In previous studies, geometrical and optical isomers of mono- and dispiroferrocenylphosphazenes were produced, and their chirality was investigated using ^{31}P-NMR spectroscopy and X-ray crystallography (19, 20). Langmuir-Blodgett thin films, DNA interactions, and the cytotoxic and antimicrobial activities of mono- and dispiroferrocenylphosphazenes were also investigated (21–23).

In this study, the reactivity of the P–Cl groups present in chlorocyclophosphazenes was taken advantage of to prepare new phosphazene derivatives. In the first step, monospiroferrocenylphosphazene derivative **1** was obtained by the reaction of hexachlorocyclotriphosphazene with potassium[3-(N-ferrocenylmethylamino)-1-propanoxide with a formula $FcCH_2NH(CH_2)_3OK$ (24). In the second step, the gradual Cl replacement reactions of compound 1 with ethyl p-hydroxybenzoate resulted in partly and fully substituted phosphazene derivatives (25). The structures of the synthesized products were characterized using elemental analysis, FTIR and Nuclear Magnetic Resonance (^{31}P-, ^{13}C- and ^{1}H-NMR) techniques. The solid-state structures of the two phosphazene derivatives (**2** and **5**) were investigated by X-ray crystallography.

MATERIAL AND METHODS

Reagents used for synthesis

Hexachlorocyclotriphosphazatriene (phosphonitrilicchloride) (Aldrich); ethyl p-hydroxybenzoate, (Aldrich) and ferrocenecarboxaldehyde (Acros organics) were used without further purification. The solvents (THF, ethanol, toluene, n-hexane, acetonitrile, and benzene) were dried by standard methods. Reactions have been monitored with TLC (Merck silica gel 60 B254 sheets). The column chromatography was performed on Merck silica gel 60 (0.040−0.063 mm).

Physical measurements

Melting points were measured with a Gallenkamp apparatus using a capillary tube. The ^{1}H, ^{13}C and ^{31}P NMR spectra were recorded on a Bruker DPX FT-NMR (300 MHz) spectrometer (SiMe4 as internal and 85% H_3PO_4 as external standards). The IR spectra were recorded on Perkin Elmer FTIR spectrometer (4000-650 cm^{-1}).

X-ray crystallography

Suitable crystals of **2** and **5** were selected for data collection which was performed on a D8-QUEST diffractometer equipped with a graphite-monochromatic Mo-Kα radiation. The structures were solved by direct methods using SHELXS-97 (26) and refined by full-matrix least-squares methods on F2 using SHELXL-2013 (27). All non-hydrogen atoms were refined with anisotropic parameters. The following procedures were implemented in our analysis: data collection: Bruker APEX2 (28); program used for molecular graphics were as follows: MERCURY programs (29); software used to prepare material for publication: WinGX (30).

Synthesis of compounds

The spiroferrocenylphosphazene derivative **1** was synthesized from the reactions of hexachlorocyclotriphosphazene with potassium salt of [3-(N-ferrocenylmethylamino)-1-propanoxide according to the literature (24).

*Synthesis of compound **2***; A solution of ethyl p-hydroxybenzoate (0.325 g, 1.95 mmol) in dry THF (100 mL) was added to a solution of **1** (1.00 g, 1.95 mmol) with K_2CO_3 (1.08 g) in dry THF (100 mL). Reaction mixture was refluxing for 12 h with stirring. Reaction mixture was purified by column chromatography with benzene used as eluent. The product eluted was mono-ethyl p-hydroxybenzoate substituted derivative **2** (0.499 g, 1.95 mmol, 37.7%, mp 146-147 ^{0}C). Anal. Calcd for **2** $C_{23}H_{26}N_4O_4FeP_3Cl_3$: C, 40.77; H, 3.87; N, 8.27. Found: C, 40.55; H, 3.93; N, 8.14. FTIR (cm^{-1}): 3098 (C-H arom.), 2906 (C-H aliph.), 1711 (C=O), 1598; 1500 (C=C arom.), 1200 (P=N).

*Synthesis of compounds geminal- (**3a**) and nongeminal- (**trans^{a}-3b**, **trans^{b}-3c** and **cis-3d**)*; The work-up procedure was similar to that of compound **2**, using **1** (1.00 g, 1.95 mmol), ethyl p-hydroxybenzoate (0.65 g, 3.90 mmol) and K_2CO_3 (1.58 g). Reaction mixture was purified by column chromatography with benzene/THF (80/1). The disubstituted compounds were not separated but they have been identified by ^{31}P-NMR spectrum from different elusion. [geminal (**3a**); non-geminal (***trans*^{a}-3b**, ***trans*^{b}-3c** and ***cis*-3d**)] (0.60 g, 40.8%). Anal. Calcd for mixture of **3a, *trans*^{a}-3b**, ***trans*^{b}-3c** and ***cis*-3d** $C_{32}H_{35}N_4O_7FeP_3Cl_2$: C, 47.61; H, 4.37; N, 6.94. Found: C, 48.39; H, 4.84; N, 6.66. FTIR (cm-1): 3083 (C-H arom.), 2980; 2981; 2934; 2853 (C-H aliph.), 1714 (C=O), 1601; 1502 (C=C arom.), 1198 (P=N).

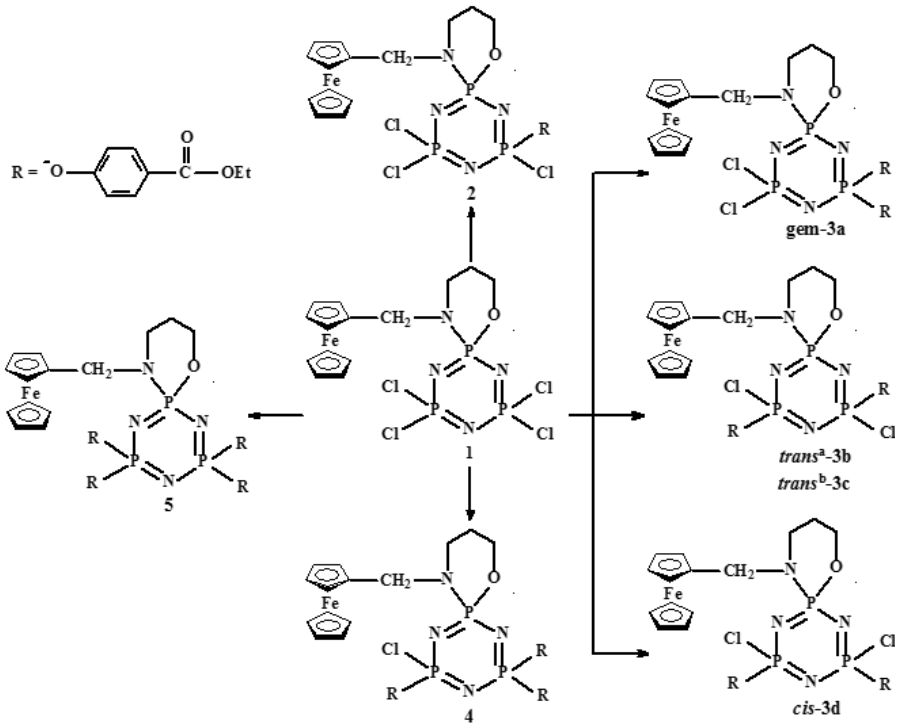
*Syntheses of compounds **4** and **5***; The work-up procedure was similar to that of compound **2**,

using **1** (0.70 g, 1.36 mmol), ethyl p-hydroxybenzoate (0.70 g, 4.21 mmol) and K_2CO_3 (2.30 g). The tri- **4** (0.41 g, 35.9%, mp 89-90 ^oC) and tetra- **5** substituted (0.23 g, 17%, mp 110-111 ^oC) compounds were purified from reaction mixture by column chromatography (benzene/THF (30/1)). Anal. Calcd for **4** $C_{41}H_{44}N_4O_{10}FeP_3Cl$: C, 52.55; H, 4.73; N, 5.98. Found: C, 51.88; H, 4.51; N, 5.85. FTIR (cm-1): 3082 (C-H arom.), 2982; 2903 (C-H aliph.), 1716 (C=O), 1601; 1501 (C=C arom.), 1199 (P=N). Anal. Calcd for **5** $C_{50}H_{53}N_4O_{13}FeP_3$: C, 56.29; H, 5.01; N, 5.25. Found: C, 56.07; H, 5.19; N, 4.86. FTIR (cm^{-1}): 3082 (C-H arom.), 2981; 2936 (C-H aliph.), 1709 (C=O), 1600; 1501 (C=C arom.), 1198 (P=N).

RESULTS AND DISCUSSION

Synthesis

The precursor molecule spirocyclicferrocenylphosphazene **1**, which has four P–Cl bonds, was synthesized according to the procedure (24). The reactivity of the P–Cl groups was then used to produce mono- **2**, di- [geminal (**3a**); non-geminal (***trans*[a]-3b, *trans*[b]-3c** and ***cis*-3d**)], tri- **4** and tetra- **5** substituted phosphazene derivatives (**Scheme 1**).



Scheme 1. The synthesis route of compounds mono- **2**, di- [geminal (**3a**); non-geminal (**trans[a]-3b**, **trans[b]-3c** and **cis-3d**)], tri- **4** and tetra- **5**.

The reaction of a 1:1 molar ratio of compound **1** and ethyl p-hydroxybenzoate produced the corresponding monosubstituted phosphazene **2** as a major product and disubstituted phosphazenes as minor products. These minor products, which were observed by TLC, were separated from the major product by chromatographic methods. The reaction of a 1:2 mol ratio of compound **1** and ethyl p-hydroxybenzoate produced the expected disubstituted phosphazenes. Disubstituted phosphazenes were not separated from the reaction mixture using chromatographic methods. When the ^{31}P-NMR analyses of two different samples taken from the column were examined, geminal- **3a** and nongeminal- (***trans*[a]-3b, *trans*[b]-3c** and ***cis*-3d**) isomers were observed. When a 1:3.3 mol ratio of compound **1** and ethyl p-hydroxybenzoate was used in the reaction, tri-substitute **4** and tetra-substitute **5** phosphazenes were synthesized. Compound **2** was crystallized from an acetonitrile/THF mixture (5:1); compound **5** was crystallized from an n-hexane/ THF mixture (10:1) at room temperature.

Spectroscopic Analysis

The ^{1}H-decoupled ^{31}P-NMR spectral data for mono- **2**, di- [geminal (**3a**); non-geminal (***trans*^{a}-3b, *trans*^{b}-3c** and ***cis*-3d**)], tri- **4** and tetra- **5** are listed in **Table 1**. The ^{31}P-NMR signals of all compounds were found on the NMR spectrum (**Figure 1-3**). Disubstituted phosphazene isomers [geminal (**3a**); non-geminal (***trans*^{a}-3b, *trans*^{b}-3c** and ***cis*-3d**)] could not be purified from the reaction mixtures using column chromatography. When the ^{31}P-NMR spectrum of two different samples obtained by column chromatography were analyzed, *cis*- and *trans*- isomers were observed in first sample while geminal isomers as well as *cis*- and *trans*- isomers were observed in the second sample. The mono- **2**, geminal- **3a** and tri- **4** substituted phosphazene derivatives showed a 12-line resonance pattern consisting of a doublet of doublets for all the P atoms. ***Trans*^{a}-3b** and ***trans*^{b}-3c** have three stereogenic P-centers, exhibiting a total of 16 signals, and indicating that ***trans*^{a}-3b** and ***trans*^{b}-3c** are diastereoisomers (9). The nongeminal-***cis* 3d** and tetra-substituted ferrocenylphosphazene **5** gave rise to one triplet and one doublet.

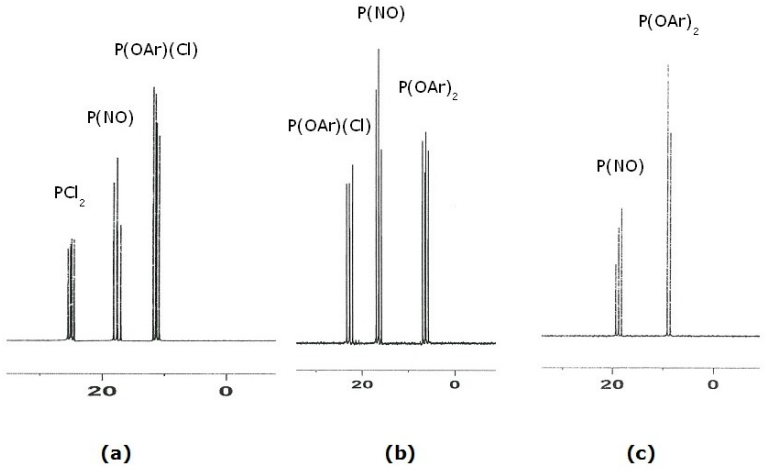


Figure 1. The ^{31}P{1H} NMR spectra of mono- **2 (a)**, tri- **4 (b)** and tetra- **5 (c)** substituted phosphazenes, respectively.

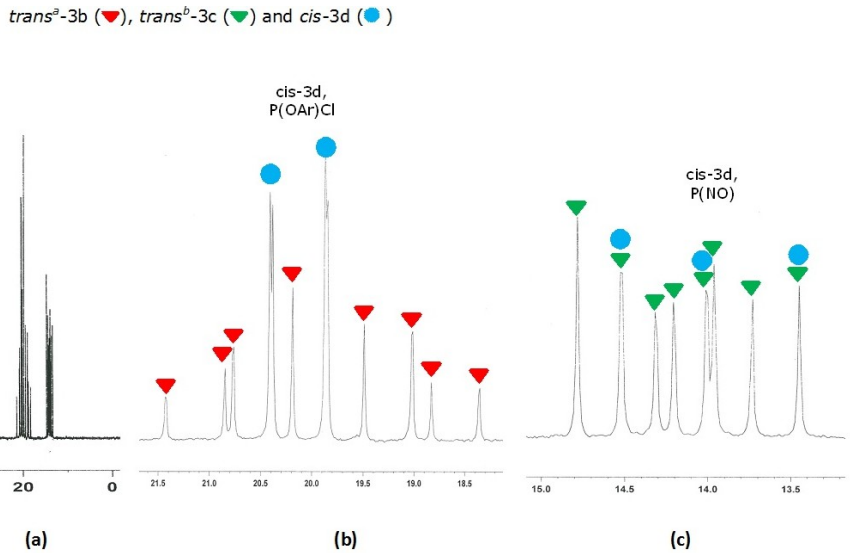


Figure 2. (a) The ^{31}P-NMR spectra of the mixture of ***trans*^{a}-3b, *trans*^{b}-3c** and ***cis*-3d**; **(b)** 21.5-18.0 ppm; **(c)** 15.0-13.0 ppm.

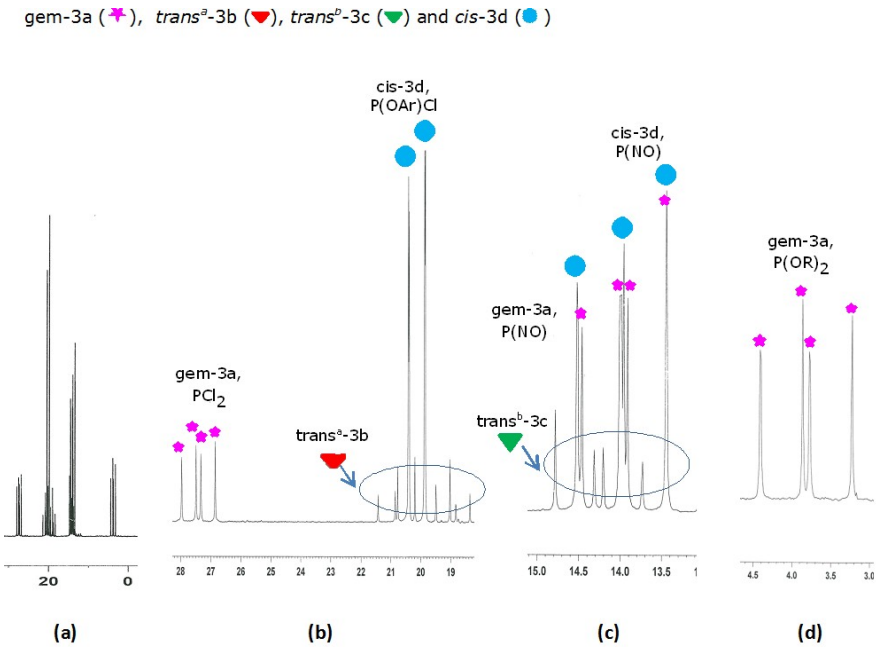
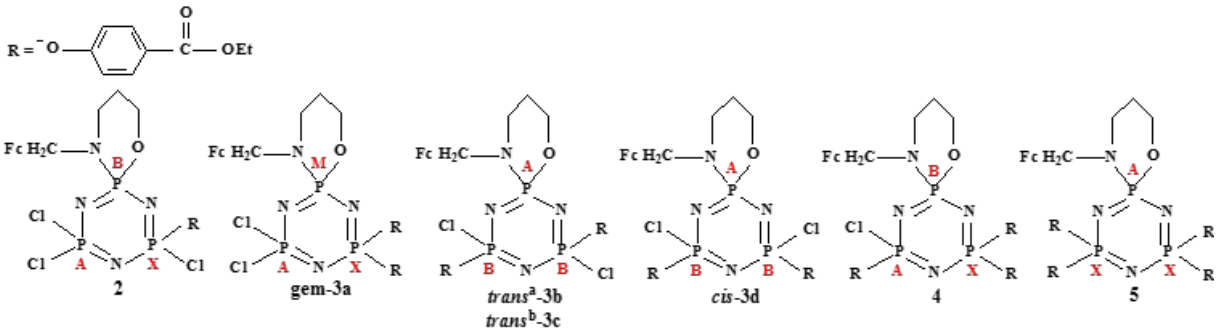


Figure 3. (a) The ^{31}P-NMR spectra of the mixture of ***gem*-3a, *trans*[a]-3b, *trans*[b]-3c** and ***cis*-3d**; **(b)** 28.0-18.0 ppm; **(c)** 15.0-13.0 ppm; **(d)** 4.5-3.5 ppm.

Table 1. The ^{31}P-NMR (decoupled) spectral data of mono- **2**, di- [geminal (**3a**); non-geminal (***trans*[a]-3b, *trans*[b]-3c** and ***cis*-3d**)], tri- **4** and tetra- **5**. (Chemical shifts are reported in ppm and J values in Hz; ^{31}P-NMR measurements in $CDCl_3$ solutions at 293 K)



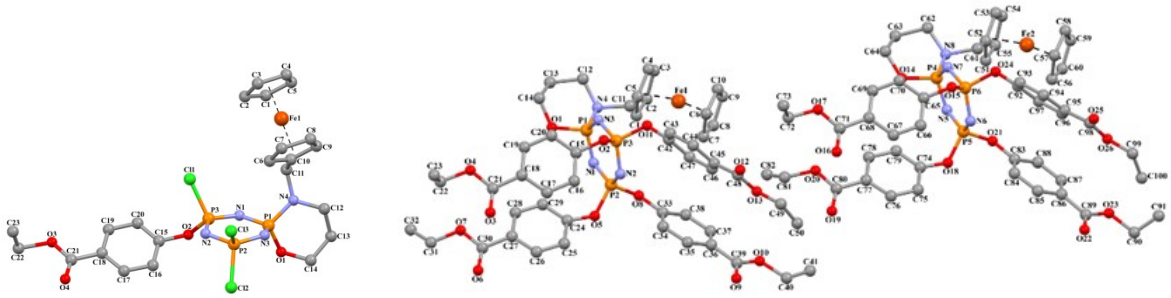
Compound	δ (ppm)				$^2J_{PP}$ (Hz)	Spin System
	PCl_2	$P(NO)_{(spiro)}$	$P(OAr)_2$	P(OAr)(Cl)		
2	25.24 (dd)	17.65 (dd)	-	11.53 (dd)	72.9; 47.4; 66.8	ABX
***gem*-3a**	27.41 (dd)	13.95 (dd)	3.83 (dd)	-	77.8; 65.6; 58.3	AMX
***trans*[a]-3b**	-	20.76	-	19.16	76.5	AB_2
***trans*[b]-3c**	-	14.31	-	13.87	43.7	AB_2
***cis*-3d**	-	13.99 (t)	-	20.13 (d)	65.6	AB_2
4	-	16.49 (dd)	6.38 (dd)	22.72 (dd)	85.1; 72.9; 65.6	ABX
5	-	18.78 (t)	8.58 (d)	-	69.3	AX_2

The expected signals from the carbon atoms and hydrogen atoms were present in the ^{13}C and ^{1}H NMR spectra (**Table S1** and **S2**) of all the new compounds. The carbon peaks for the carbonyl ($\underline{C}OCH_2CH_3$) and phenyl groups in the ethyl benzoate groups were observed ranging from 165.84 to 165.70 ppm and from 154.51 to 120.75 ppm, respectively. Also, the carbon peaks for the ferrocenyl group were observed in a range from 82.47 to 67.15 ppm as expected.
All the synthesized substituted phosphazenes have aliphatic protons that are diastereotopic, so the ^{1}H-NMR spectra of the new compounds are highly complex. When the ^{1}H-NMR spectra of the synthesized compounds were examined, three different peaks were observed for the H2, H3 and H4 protons of the ferrocenyl group at 3.92 to 4.31 ppm. The protons of H4 are equivalent and were observed as a single peak. The H6 protons belonging to the substituent were observed as quadrupole peaks at 4.25 to 4.44 ppm, and the H7 protons were observed as triple peaks at 1.35 to 1.44 ppm. The H2 and H3 protons of the aromatic rings were observed in the range from 7.20 to 8.17 ppm.

The IR spectra of the new phosphazene derivatives displayed characteristic bands between 1200 and 1198 cm^{-1} and between 1174 and 1169 cm^{-1}. These vibration bands were attributed to the stretching frequencies (asymmetric and symmetric) of the P–N bonds in the phosphazene rings. At the same time the substitute ethyl p-hydroxybenzoate groups have characteristic IR absorbance peaks in the range from 1709 to 1716 cm^{-1} due to the stretching of the C=O bonds.

X-ray structures of compounds 2 and 5

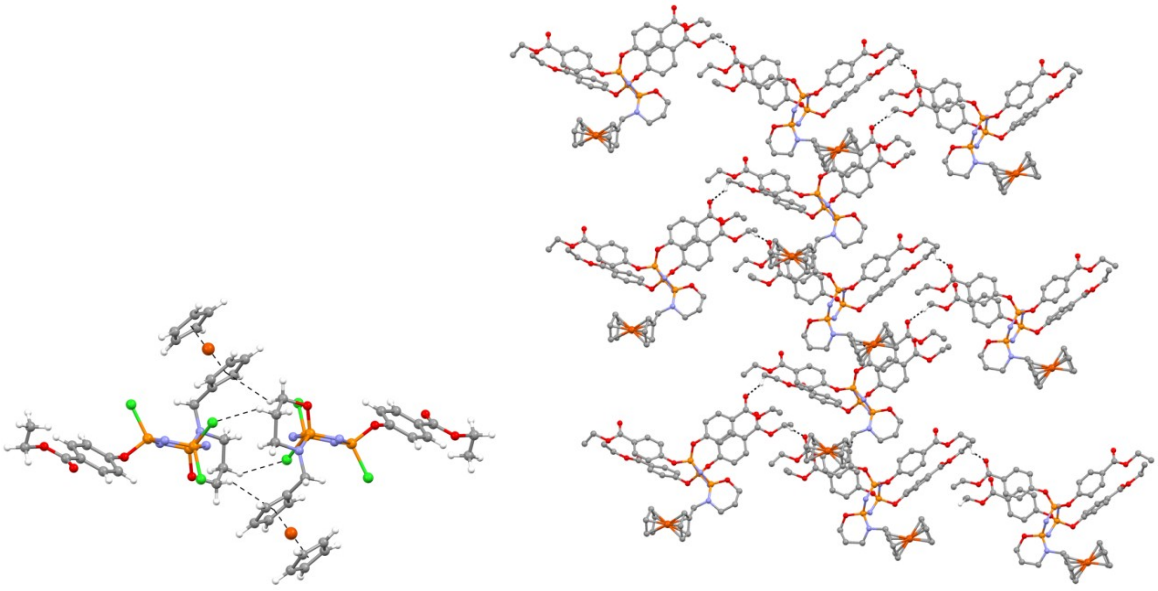
The molecular structures of **2** and **5**, with the atom numbering schemes, are shown in **Figure 4**. The crystallographic data are given in **Table S3**, and the selected bond lengths and angles are listed in **Table S4** for compounds **2** and **5**. The crystallographic analyses reveal that compounds **2** and **5** are very similar. Compound **2** crystallizes in the space group $P2_1/c$, while compound **5** crystallizes in the space group Pn.



(a) (b)

Figure 4. The molecular structures of **2** (a) and **5** (b) showing the atom numbering schemes.

In compound **2**, the phosphazene ring is in a flattened-boat conformation [φ = −62.7(3)° and θ = 60.2(3)°] having a total puckering amplitude QT of 0.180(1) Å. In compound **5**, the values of the ring puckering parameters are φ = 191 (2) to 196 (3)°, θ = 78.3 (3) to 80.0 (3)° and QT = 0.121 to 0.114 (5) Å, indicating that each phosphazene ring has a chair conformation. The P1/O1/C12-C14/N4 ring was in a chair conformation [φ = 36.5(1)° and θ = 89.6(1)°] having a total puckering amplitude QT of 0.659(2) Å in **2**, while in **5**, the values of the ring puckering parameters were φ = 191(2) to 196(3)°, θ = 78.3(3) to 80.0(3)° and QT = 0.121(4) to 0.114(5) Å. In the phosphazene rings, the P–N bond lengths were in the range of 1.561(3) to 1.612(3) Å [average value is 1.582(3) Å] (**Table S4**).



(a) **(b)**

Figure 5. The C-H···Cl hydrogen bonds and C-H···π interactions in the compound **2 (a)**; **5b.** an infinite 1D supramolecular network in the compound **5 (b)**.

As shown in **Figure 5**, the C–H···Cl hydrogen bonds produced a centrosymmetric $R_2^2(14)$ ring in **2 (a)**, while the intermolecular C–H···O hydrogen bonds produced a 1D supramolecular network running parallel to the [101] direction in **5** (**b**). Compounds **2** and **5** also contain C–H···π (**Table 2**) and π···π interactions. Each π···π contact between the ferrocenyl rings may stabilize the structure, with a center to center distance of 3.287(2) Å in **2** and 3.303(6) and 3.308(6) Å in **5**.

Table 2. The hydrogen bonds and C-H···π interactions parameters for compounds **2** and **5** (Å, º)

D-H· · ·A	D-H	H···A	D···A	D-H···A
Compound 2				
C13-H13A···Cl3^{i}	0.99	2.77	3.649 (4)	148
C14-H14A···Cg(2)^{i}	0.99	2.87	3.624	134
Compound 5				
C29—H29···N1	0.93	2.59	3.228 (11)	126
C50—H50B···O19	0.96	2.52	3.39 (2)	151
C72—H72A···O6^{i}	0.97	2.56	3.497 (19)	162
C79—H79···N5	0.93	2.58	3.221 (12)	126
C84—H84···N6	0.93	2.61	3.163 (11)	119
C13-H13A···Cg(1)^{i}	0.97	2.92	3.661 (13)	134
C62-H62B···Cg(2)^{ii}	0.97	2.93	3.710 (13)	138

Symmetry codes: (i) −x+1, −y, −z+1; Cg(2)=C6-C10 for **2**; (i) x−1/2, −y, z+1/2; (ii) x−1/2, 1−y, z+1/2; Cg(1)=C33-C38; Cg(2)=C83-C88 for **5**.

CONCLUSIONS

The Cl replacement reactions of monoferrocenylphosphazene **1**, which has four P–Cl bonds with ethyl benzoate, resulted in the formation of new cyclotriphosphazene derivatives: [mono- **2**, di- [geminal (**3a**); nongeminal (***trans***^{a}**-3b,** ***trans***^{b}**-3c** and ***cis*-3d**)], tri- **4** and tetra- **5**]. The structures of these new compounds were characterized using elemental analyses, FTIR and NMR (^{1}H-, ^{13}C- and ^{31}P-) techniques. The peaks observed in the ^{31}P-NMR spectrum were evaluated by comparison with the results obtained in previous studies. The presence of geminal (**3a**), non-geminal (***trans***^{a}**-3b,** ***trans***^{b}**-3c** and ***cis*-3d**) compounds was detected in the reaction mixtures. Furthermore, the molecular geometries of **2** (monosubstituted ferrocenylphosphazene) and **5** (tetrasubstituted ferrocenylphosphazene) were determined from the X-ray crystallography data.

REFERENCES

1. Chandrasekhar V, Narayanan RS, Mamidala R, Venkatasubbaiah K. Phosphazenes. In Organophosphorus Chemistry Volume 47, Eds. Allen, DW, Loakes, D and Tebby, JC. Royal Society of Chemistry, Cambridge, UK; 2018, 363-424.

2. Stewart FF. Phosphazenes. In Organophosphorus Chemistry Volume 44, Eds. : Allen DW, Loakes D, Tebby JC. Royal Society of Chemistry, Cambridge, UK; 2015, 397-430.

3. Chandrasekhar V, Krishnan V. Advances in the chemistry of chloro-cyclophosphazenes. Advances in Inorganic Chemistry. 2002;53:159-211.

4. Beşli S, Coles SJ, Coles LS, Davies DB, Kılıç A. Investigation of a spiro to ansa rearrangement with di-functional alcohols in cyclotriphosphazene derivatives. Polyhedron. 2012;43:176–84.

5. Türe S. Phosphorus-nitrogen compounds: Reinvestigation of the reactions of hexachlorocyclotriphosphazene with 1,4-butane- and 1,6-hexane-diols—NMR studies of the products. Phosphorus, Sulfur, and Silicon and the Related Elements. 2016;191(8): 1174-82.

6. Muralidharan K, Elias A. Preparation of the First Examples of Ansa−Spiro Substituted Fluorophosphazenes and Their Structural Studies: Analysis of C−H···F−P Weak Interactions in Substituted Fluorophosphazenes. Inorg. Chem. 2003;42:7535–43.

7. Koran K, Tekin Ç, Biryan F, Tekin S, Sandal S, Görgülü AO. Synthesis, structural and thermal characterizations, dielectric properties and in vitro cytotoxic activities of new 2,2,4,4-tetra(4'-oxy-substituted-chalcone)-6,6-diphenylcyclotriphosphazene derivatives. Medicinal Chemistry Research. 2017;26(5):962-74.

8. Tümer Y, Şehirli E, Yüksektepe Ataol Ç. Syntheses and Structural Characterizations of First Paraben Substituted Ferrocenyl Phosphazene Compounds. JOTCSA. 2017;4(1):299-312.

9. Tümer Y, Koç LY, Asmafiliz N, Kılıç Z, Hökelek T, Soltanzade H, Açık L, Yola ML, Solak AO. Phosphorus–nitrogen compounds: Part 30. Syntheses and structural investigations, antimicrobial and cytotoxic activities and DNA interactions of vanillinato-substituted NN or NO spirocyclic monoferrocenyl cyclotriphosphazenes. J. Biol. Inorg. Chem. 2015;20:165-78.

10. Kundu A, Hariharan PS, Prabakaran K, Anthony SP. Synthesis of new colori/ A fluorimetric chemosensor for selective sensing of biologically important Fe3+, Cu2+ and Zn2+ metal ions. Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy. 2015;151:426–31.

11. Yenilmez Çiftçi G, Şenkuytu E, Bulut M, Durmuş M. Novel Coumarin Substituted Water Soluble Cyclophosphazenes as "Turn-Off" Type Fluorescence Chemosensors for Detection of Fe3+ ions in Aqueous Media. Journal of Fluorescence. 2015;25:1819–30.

12. Şenkuytu E. Novel Aminopyrene Substituted Monospiro/Dispiro Cyclotriphosphazenes: Synthesis, Characterization and Chemosensor Properties. Celal Bayar University Journal of Science. 2018;14(2):209–16.

13. Sudhakar S, Sellinger A. Nanocomposite Dendrimers Based on Cyclic Phosphazene Cores: Amorphous Materials for Electroluminescent Devices. Macromolecular Rapid Communications. 2006;27(4):247-54.

14. Bolink HJ, Santamaria GS, Sudhakar S, Zhenb C, Sellinger A. Solution processable phosphorescent dendrimers based on cyclic phosphazenes for use in organic light emitting diodes (OLEDs). Chemical Communications. 2008;5:618-20.

15. Schrögel P, Hoping M, Kowalsky W, Hunze A, Wagenblast G, Lennartz C, Stohrieg P. Phosphazene-Based Host Materials for the Use in Blue Phosphorescent Organic Light-Emitting Diodes. Chemistry of Materials. 2011;23(22):4947-53.

16. Soh SM, Santamaria SAG, Perez-Morales M, Bolink HJ, Sellinger A. Solution processable high band gap hosts based on carbazole functionalized cyclic phosphazene cores for application in organic light-emitting diodes. Journal of Polymer Science Part B. 2011;49(7):531-9.

17. Wang L, Yang YX, Shi X, Mignani S, Caminade AM, Majoral JP. Cyclotriphosphazene core-based dendrimers for biomedical

applications: an update on recent advances. Journal of Materials Chemistry B. 2018;6:884-95.

18. Caminade AM, Hameauab A and Majoralab JP. The specific functionalization of cyclotriphosphazene for the synthesis of smart dendrimers. Dalton Transactions. 2016;5:1810-22.

19. Tümer Y, Asmafiliz N, Zeyrek CT, Kılıç Z, Açık L, Çelik SP, Türk M, Çağdaş Tunalı B, Ünver H, Hökelek T. Syntheses, spectroscopic and crystallographic characterizations of cis- and trans-dispirocyclic ferrocenylphosphazenes: molecular dockings, cytotoxic and antimicrobial activities. New J. Chem. 2018;42(3):1740-56.

20. Tümer Y, Asmafiliz N, Kılıç Z, Aydın B, Açık L, Hökelek T. Phosphorus-nitrogen compounds: Part 43. Syntheses, spectroscopic characterizations and antimicrobial activities of cis- and trans-N/O dispirocyclotriphosphazenes containing ferrocenyl pendant arms. J. Mol. Struct. 2018;1173:885-93.

21. Elmas G, Okumuş A, Cemaloğlu R, Kılıç Z, Çelik SP, Açık L, Tunalı BÇ, Türk M, Çerçi NA, Güzel R, Hökelek T. Phosphorus-nitrogen compounds. part 38. Syntheses, characterizations,cytotoxic, antituberculosis and antimicrobial activities and DNA interactions of spirocyclotetraphosphazenes with bis-ferrocenyl pendant arms. Journal of Organometallic Chemistry. 2017;853:93-106.

22. Asmafiliz N, Civan M, Uzunalioğlu N, Özben A, Kılıç Z, Kayalak H, Açık L, Hökelek T. Phosphorus-nitrogen compounds. Part 41. Ferrocenyl pendant-armed spirocyclopiperidinocyclotriphosphazatrienes; Langmuir-Blodgett thin films and biological activity studies. J. Chem. Sci. 2018;130:152.

23. Asmafiliz N, Kılıç Z, Civan M, Avcı O, Gönder LY, Açık L, Aydın B, Türk M and Hökelek T. Phosphorus–nitrogen compounds. Part 36. Syntheses, Langmuir–Blodgett thin films and biological activities of spiro-bino-spiro trimeric phosphazenes. New J. Chem. 2016;40:9609-26.

24. Asmafiliz N, Kılıç Z, Öztürk A, Hökelek T, Koç LY, Açık L, Kısa Ö, Albay A, Üstündağ Z, Solak AO. Phosphorus-Nitrogen Compounds : Part 18. Syntheses, Stereogenic Properties, Structural and Electrochemical Investigations, Biological Activities and DNA Interactions of New Mono- and Bis-Ferrocenyl Spirocyclic Phosphazene Derivatives. Inorg. Chem. 2009;48:10102-16.

25. Çayırbaşı M. Etil p-hidroksibenzoat sübstitüe ferrosenilfosfazen türevlerinin sentezi ve yapılarının aydınlatılması, [Yüksek Lisans Tezi]. [Karabük]: Karabük Üniversitesi; 2013.

26. Sheldrick GM, Acta Cryst. 2008; A64: 112.

27. Sheldrick GM, Acta Cryst. 2015; C71: 3.

28. APEX2, Bruker AXS Inc. Madison Wisconsin USA. 2013.

29. Mercury, version 3.3; CCDC, available online via cdc.cam.ac.uk/products/mercury.

30. Farrugia LJ, J. Apply. Cryst. 1999; 32: 837.