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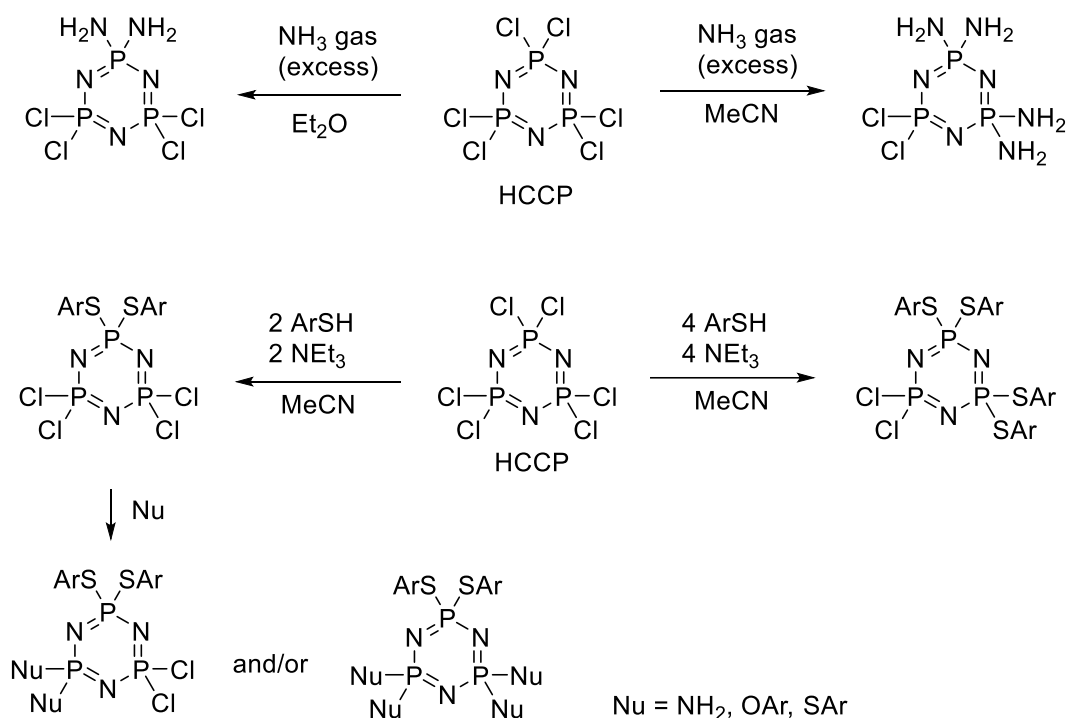
**SYNTHESIS OF 2-ARYLOXY-2,4,4,6,6-PENTACHLORO-CYCLOTRIPHOSPHAZENES ( $N_3P_3Cl_5(OAr)$ ): MONOARYLOXYLATION OF HEXACHLORO-CYCLOTRIPHOSPHAZENE ( $N_3P_3Cl_6$ ) AND MASS SPECTRA OF CHLORO-CYCLOTRIPHOSPHAZENE DERIVATIVES. DIFFERENCE BETWEEN EI VS. ESI METHODS**

**Manabu Kuroboshi,\* Ryota Takahashi, and Hideo Tanaka**

Tsushima-naka 3-1-1, Kita-ku, Okayama, Okayama, JAPAN,  
mkurohos@cc.okayama-u.ac.jp

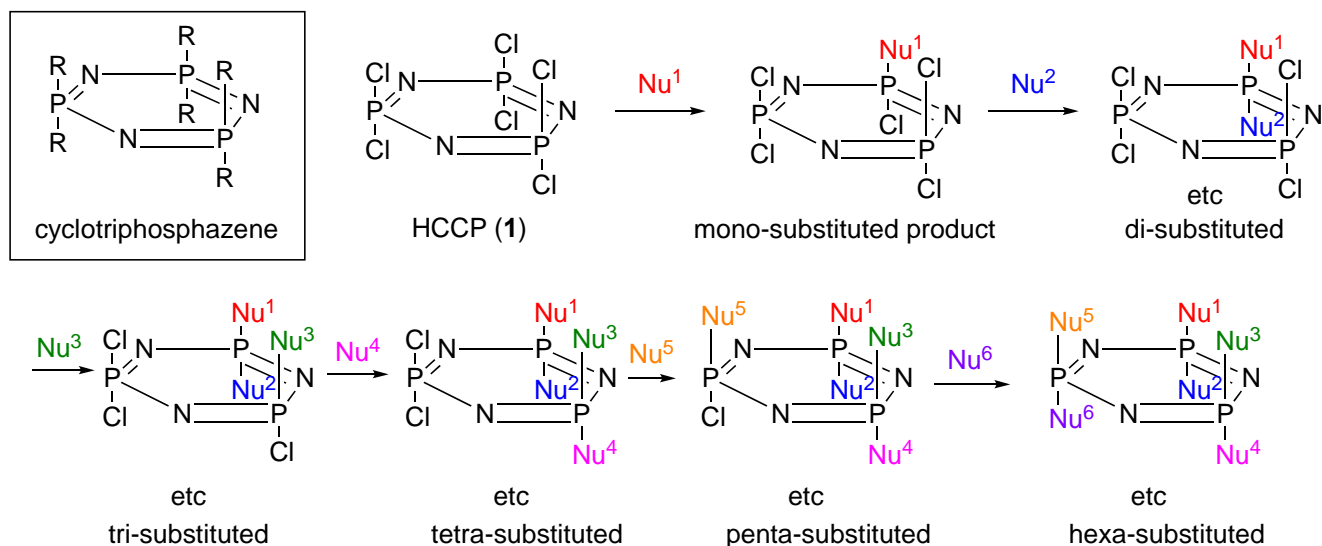
**Abstract** – Hexachlorocyclotriphosphazene (HCCP,  $N_3P_3Cl_6$ ) was treated with Li aryloxide in THF at  $-40\text{ }^\circ\text{C}$  to give monoaryloxy pentachlorocyclotriphosphazene ( $N_3P_3Cl_5(ArO)$ ) selectively.  $N_3P_3Cl_5(ArO)$  did not give further aryloxyated products  $N_3P_3Cl_{6-n}(ArO)_n$  ( $n \geq 2$ ) under the same reaction conditions. In mass spectra (MS) of  $N_3P_3Cl_5(ArO)$ ,  $[N_3P_3Cl_5(ArO)]^+$  were detected by EI method, whereas partially hydrated products  $[N_3P_3Cl_4(ArO)(O^-)]$  were detected instead of  $[N_3P_3Cl_5(ArO)]^+$  by ESI method.

Hexachlorocyclotriphosphazene (HCCP),  $N_3P_3Cl_6$  (**1**), has a flat six-membered ring in which three N atoms and three P atoms are connected alternately and two Cl atoms connected on each P atom.<sup>1</sup> Since the Cl-P bond of HCCP is easily substituted with nucleophiles, multi-functionalized materials can be easily prepared when multi-types of nucleophiles are introduced. To prepare multi-functionalized cyclotriphosphazene derivatives, partial substitution of HCCP would be an important and fundamental method. We reported gaseous  $NH_3$  (excess) was allowed to react with HCCP to afford 2,2-diamino-4,4,6,6-tetrachlorocyclotriphosphazene and/or 2,2,4,4-tetraamino-6,6-dichlorocyclotriphosphazene,<sup>2</sup> and arylthiol  $ArSH/NEt_3$  gave 2,2-bis(arylthio)-4,4,6,6-tetrachlorocyclotriphosphazene and 2,2,4,4-tetrakis(arylthio)-6,6-dichlorocyclotriphosphazene.<sup>3</sup> We also reported nucleophilic substitution of 2,2-bis(arylthio)-4,4,6,6-tetrachlorocyclotriphosphazenes (Scheme 1).<sup>4</sup>



Scheme 1. Substitution reactions of HCCP

The most direct method to prepare multi-functionalized cyclotriphosphazenes would be introduction of nucleophiles one by one (Scheme 2).

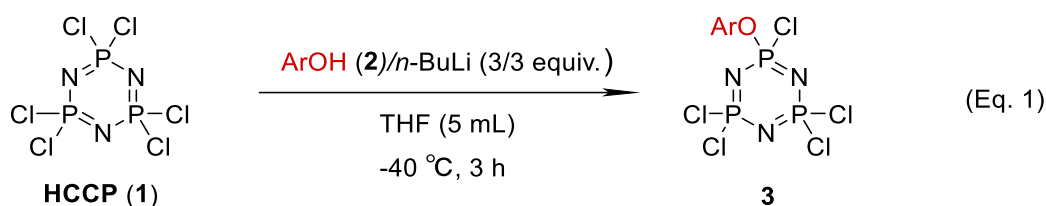


Scheme 2. Stepwise synthesis of hexa-substituted HCCP

Dell *et al.* reported reaction of HCCP with phenoxide.<sup>5</sup> They treated HCCP with NaOPh in THF at  $-78^\circ\text{C}$ . 1 equiv. of NaOPh gave mono-substituted product, whereas 2 equiv. of NaOPh gave a mixture of di-substituted and tri-substituted products (72%, and 10%, respectively). 3 and 4 equiv. of NaOPh

gave tri-substituted (52%) and tetra-substituted products (71%), respectively. Though they isolated the products by distillation, column chromatography and/or recrystallization, they did not analyze the reaction mixture by  $^{31}\text{P}$  NMR to reveal the product distribution. Allock *et al.* also reported reaction between HCCP and steroid salts.<sup>6</sup> They also obtained multi-substituted products.

In this paper, we report mono-aryloxylation of HCCP **1** with excess amount of phenols **2**/*n*-BuLi to give mono(aryloxy)pentachlorocyclotriphosphazene derivatives **3** (Eq. 1). We also report a unique behavior of **3** in mass spectrometry.



Firstly, we examined the effects of counter cations (Table 1). To a THF (5 mL) solution of *p*-methoxyphenol (**2a**, 0.5 mmol) was added hexane solution of *n*-BuLi (1.57 M, 0.32 mL, 0.5 mmol) dropwise at -40 °C to give Li salt of **2a**. The mixture was stirred at the same temperature for 1 h. To the reaction mixture was added HCCP (**1**, 0.5 mmol), and the whole mixture was stirred for 3 h at -40 °C. An aliquot of the reaction mixture was analyzed by  $^{31}\text{P}$  NMR to find that a mixture of mono-substituted product **3a** and **1** (54:46) was obtained and di-substituted product **4a** and tri-substituted product **5a** were not detected (Entry 1). On the other hand, Na and K salts of **2a**, prepared from **2a** with NaH and  $\text{K}_2\text{CO}_3$ , respectively, gave a mixture of **3a**, **4a**, and **5a** (Entries 2, 3). In the latter cases, *non-gem-cis*- and *-trans*-isomers of **4a** and **5a** were detected, whereas *gem* isomers were not detected.

Next, the amount of **2a**/*n*-BuLi was examined. More than 3 equiv. of **2a** and *n*-BuLi were used, the desired product **3a** was obtained in 92% yield; neither di-substituted **4a** nor tri-substituted **5a** were detected even 6 equiv. of **2a**/*n*-BuLi were used.<sup>7,8</sup>

Solvent effects were remarkable for the aryloxylation (Table 2): We used LiOAr prepared from **2a** and LiOH<sup>9</sup> when we used DMF and acetone as a solvent (Entries 1, 2). THF (low dielectric constant) gave only **3a** (Entry 3), whereas a mixture of **3a** and **4a** was obtained in acetone (middle dielectric constant, Entry 2), and **5a** was obtained as a sole product in DMF (high dielectric constant, Entry 1) with 3 equiv. of LiOAr.

Table 1. Effect of counter cation

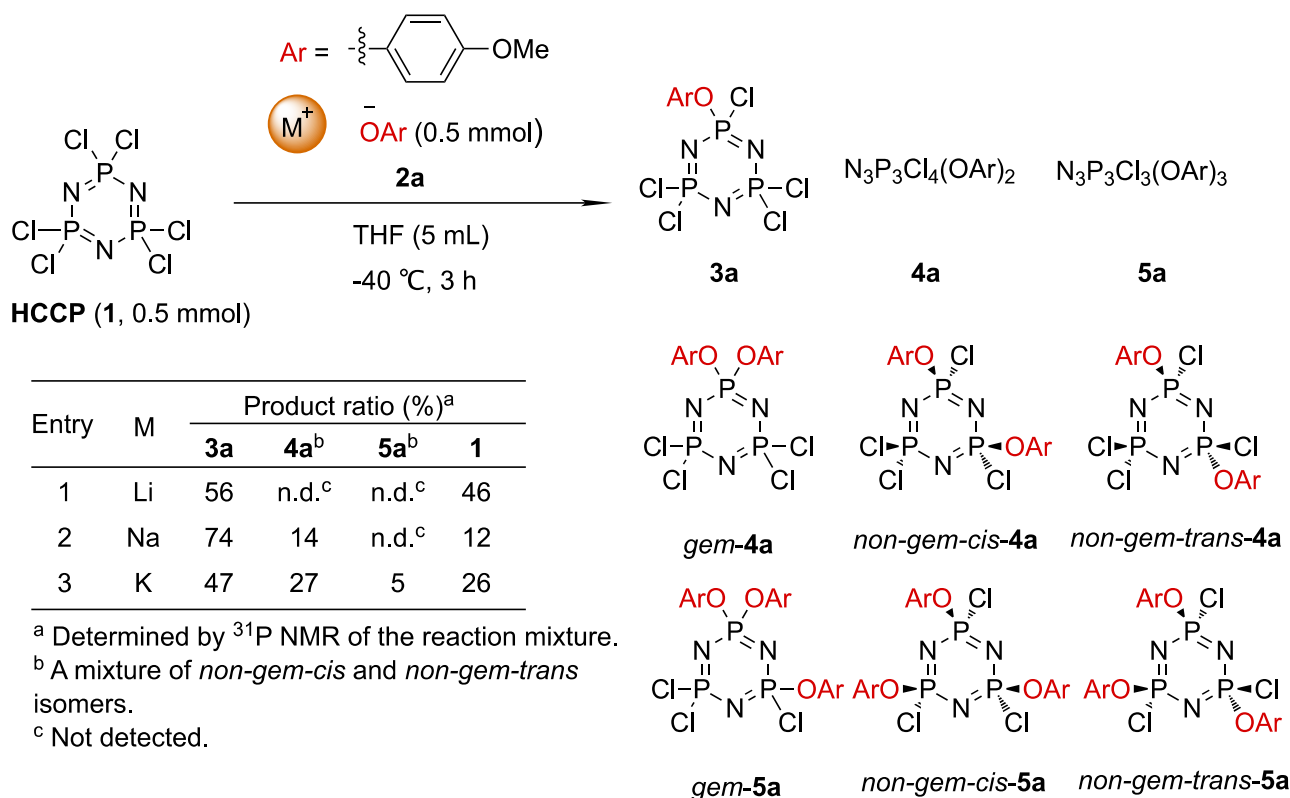
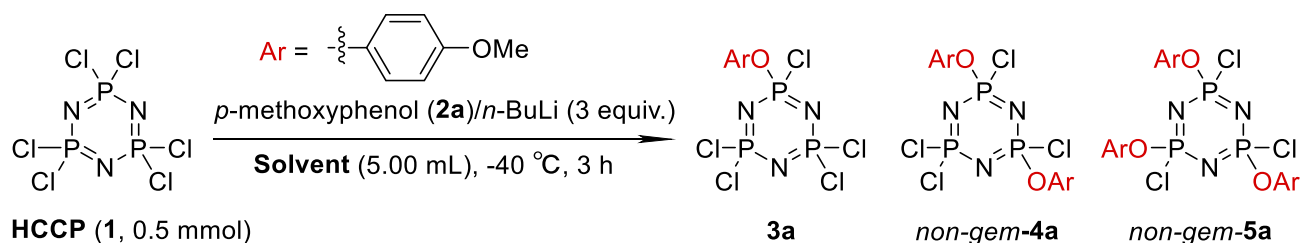
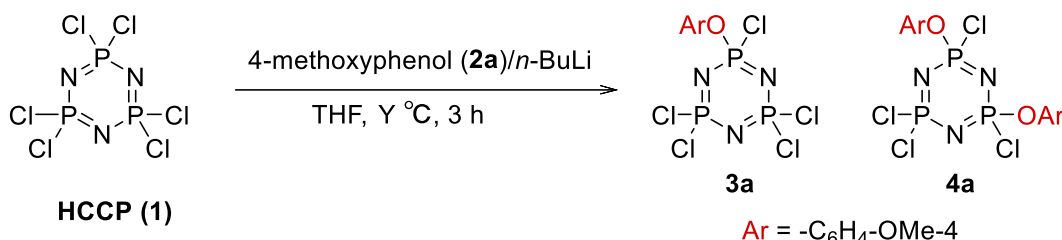


Table 2. Solvent effects

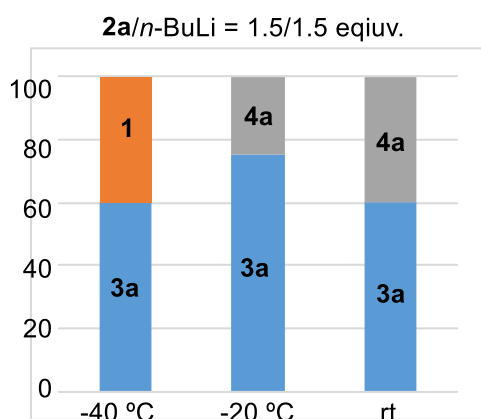


Reaction temperature was also an important factor (Figure 1a). When **1** was treated with 1.5 equiv. of 4-methoxyphenol (**2a**)/*n*-BuLi at -40 °C, the desired mono-substituted product **3a** was obtained in 60% yield

together with **1** (40%): whereas a mixture of **3a** and di-substituted **4a** was obtained (75/25% and 60/40%) at -20 °C and room temperature, respectively, and a complex mixture of unidentified products was obtained at 40 °C. The aryloxylation reaction was completed within 3 h with 3 equiv. of **2a**/*n*-BuLi (Figure 1b).

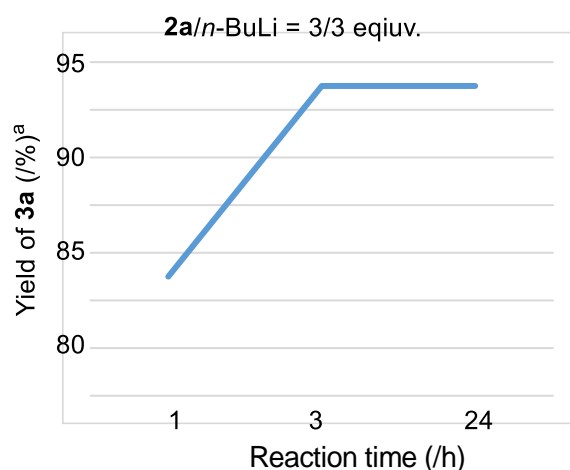


(a) Effect of reaction temperature



<sup>a</sup>Determined by <sup>31</sup>P NMR of the reaction mixture. Reaction time: 3 h. At 40 °C, a complex mixture was obtained.

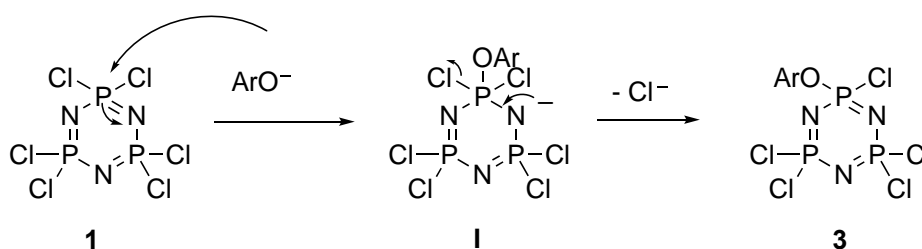
(b) Time course of the aryloxylation



<sup>a</sup>Determined by <sup>31</sup>P NMR of the reaction mixture. Reaction temperature: -40 °C,...

Figure 1. Effects of the reaction temperature and time course of the aryloxylation

From these results, the substitution reaction would proceed addition-elimination mechanism (Scheme 3), wherein reactivity of the ArO<sup>-</sup> and stability of an anionic intermediate I would be a key point. When a polar solvent and K<sup>+</sup> counter cation were used, ArOK would be solvated to give ArO<sup>-</sup>(solv)<sub>n</sub> and K<sup>+</sup>(solv)<sub>m</sub> and nucleophilicity of ArO<sup>-</sup> would be increased. The intermediate I would be stabilized in a polar solvent. As the results, multi-substitution would occur under such reaction conditions.



Scheme 3. Addition-elimination reaction of aryloxylation of HCCP (**1**)

We examined scope and limitation of this aryloxylation (Table 3). ArOH containing both electron-donating groups (Entries 1-3) and electron-withdrawing groups (Entries 4-6) gave the corresponding mono-substituted products **3a-3f**, efficiently. The structure of **3** was determined by  $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{31}\text{P}$  NMR and mass spectra (*vide infra*).

Table 3. Scope and limitation of the aryloxylation

**HCCP (1, 0.5 mmol)** + **ArOH (2)/n-BuLi (3 equiv.)** in THF (5 mL) at -40 °C, 3 h yields **3** (mono-substituted product) and **4** (di-substituted product).

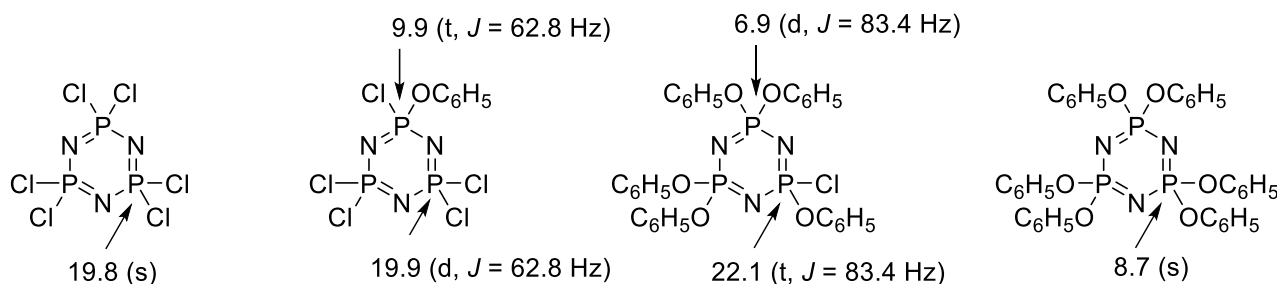
Entry	ArOH (2)	pKa of 2	Product ratio <sup>a</sup>			Isolated yield of 3	
			3	4 <sup>b</sup>	1		
1	<i>p</i> -MeOC <sub>6</sub> H <sub>4</sub> OH	<b>2a</b>	10.4	91	n.d. <sup>c</sup>	9	57
2	<i>p</i> -MeO(CH <sub>2</sub> C <sub>2</sub> O)C <sub>6</sub> H <sub>4</sub> OH	<b>2b</b>	10.24	93	n.d. <sup>c</sup>	7	42
3	<i>p</i> -MeC <sub>6</sub> H <sub>4</sub> OH	<b>2c</b>	10.21	66	n.d. <sup>c</sup>	34	46
4	<i>p</i> -FC <sub>6</sub> H <sub>4</sub> OH	<b>2d</b>	9.92	84	trace	16	84
5	<i>p</i> -ClC <sub>6</sub> H <sub>4</sub> OH	<b>2e</b>	9.47	78	9	13	56
6	<i>p</i> -NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> OH	<b>2f</b>	7.23	73	19	8	55

<sup>a</sup> Determined by  $^{31}\text{P}$  NMR of the reaction mixture.

<sup>b</sup> A mixture of *cis*- and *trans*-isomeres.

<sup>c</sup> Not detected.

To analyze structure of cyclotriphosphazene derivatives,  $^{31}\text{P}$  NMR is a powerful method. However, it is not enough because only limited numbers of the derivatives have been reported and  $^{31}\text{P}$  NMR database is insufficient. For example, in the synthesis of HCCP derivatives, number of introduced nucleophile is hardly determined by  $^{31}\text{P}$  NMR. In Figure 2,  $^{31}\text{P}$  NMR data of four cyclotriphosphazene derivatives are shown: Chemical shift of  $\text{PCl}_2$  and  $\text{P(OAr)}_2$  appeared about 20 ppm and 10 ppm, respectively, downfield from  $\text{H}_3\text{PO}_3$  (85% aq. external standard), whereas  $\text{PCl(OAr)}$  appeared in wider range, from 10 ppm to 25 ppm.

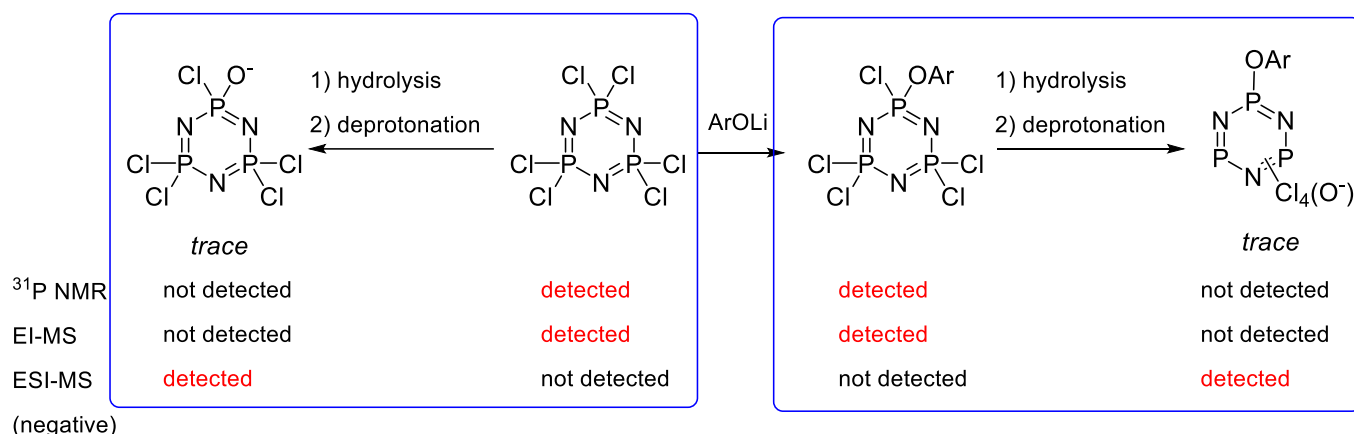
Figure 2.  $^{31}\text{P}$  NMR of cyclotriphosphazene derivatives

Since Cl has isotopes  $^{35}\text{Cl}$  and  $^{37}\text{Cl}$  in 3:1 ratio, mass spectra of the chlorinated compounds show a unique pattern of isotope peaks depending on the number of Cl atoms (Table 4).<sup>10</sup> Therefore, mass spectra would be a powerful supporting tool to determine partially-substituted HCCP derivatives: kinds of substituents and number of the substituents introduced.

Table 4. Isotope-peak pattern of chlorinated compounds

	relative intensity (%) referred to M						
	M	M+2	M+4	M+6	M+8	M+10	M+12
Cl	100	32.6					
Cl <sub>2</sub>	100	65.3	10.6				
Cl <sub>3</sub>	100	97.8	31.9	3.5			
Cl <sub>4</sub>	100	131.0	63.9	14.0	1.2		
Cl <sub>5</sub>	100	163.0	106.0	34.7	5.2	0.4	
Cl <sub>6</sub>	100	196.0	161.0	69.4	12.0	2.2	0.1

Among ionization methods, EI (electron-impact) and ESI (electrospray ionization) are frequently used for small molecules, and usually these results were consistent. ESI method uses very soft ionization, and  $\text{M}^+$  can be detected easily. On the other hand, EI method uses very hard ionization, and many fragment peaks are detected which can help to analyze sub-structure of samples. In our study of MS of chlorocyclotriphosphazene derivatives  $\text{N}_3\text{P}_3\text{Cl}_5(\text{OAr})$ , we found that EI gave  $[\text{N}_3\text{P}_3\text{Cl}_5(\text{OAr})]^+$  whereas ESI gave  $[\text{N}_3\text{P}_3\text{Cl}_4(\text{O}^-)(\text{OAr})]$  (Table 5). Mass spectrum of HCCP was measured by using EI (electron impact) ionization method to give a molecular ion peak  $\text{N}_3\text{P}_3\text{Cl}_6$  at  $m/z = 344.7443$  together with its isotope peaks. In  $^{31}\text{P}$  NMR spectrum, HCCP was detected at 20.61 ppm as a singlet peak. On the other hand, mass spectrum of HCCP by using ESI (electron shower ionization) method shows a molecular ion peak at 325.7707 ( $\text{N}_3\text{P}_3\text{Cl}_5\text{O}^-$ ) with its isotope peaks in negative mode, and no HCCP peaks were detected. Other cyclotriphosphazene derivatives  $\text{N}_3\text{P}_3\text{Cl}_{6-n}\text{R}_n$  similarly showed  $[\text{N}_3\text{P}_3\text{Cl}_{6-n}\text{R}_n]^+$  and  $\text{N}_3\text{P}_3\text{Cl}_{5-n}(\text{O}^-)\text{R}_n$  in EI- and ESI-mass spectra, respectively (Scheme 4).



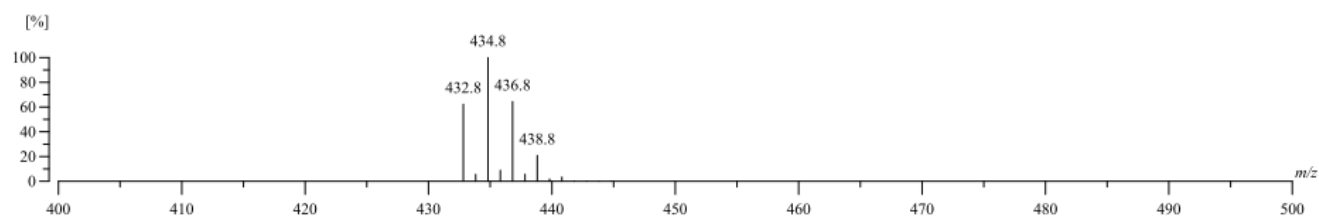
Scheme 4. <sup>31</sup>P NMR and MS identification of chlorocyclotriphosphazene derivatives

These phenomena would be explained as follows. HCCP was allowed to react with ArOLi to give  $\text{N}_3\text{P}_3\text{Cl}_5(\text{OAr})$ . To measure mass spectra,  $\text{N}_3\text{P}_3\text{Cl}_5(\text{OAr})$  was diluted in MeCN (2-3 ng/mL), and would be partially hydrolyzed to give a small amount of  $\text{N}_3\text{P}_3\text{Cl}_4(\text{OH})(\text{OAr})$  which could not be detected in <sup>31</sup>P NMR. As EI-MS is a strong ionization method,  $\text{N}_3\text{P}_3\text{Cl}_5(\text{OAr})$  would be directly ionized to give  $[\text{N}_3\text{P}_3\text{Cl}_5(\text{OAr})]^+$ . On the other hand, ESI-MS is very soft ionization method, and  $\text{N}_3\text{P}_3\text{Cl}_5(\text{OAr})$  would not be ionized efficiently, while  $\text{N}_3\text{P}_3\text{Cl}_4(\text{OH})(\text{OAr})$  can be easily ionized by deprotonation to give  $\text{N}_3\text{P}_3\text{Cl}_4(\text{O}^-)(\text{OAr})$  which can be detected in negative mode.

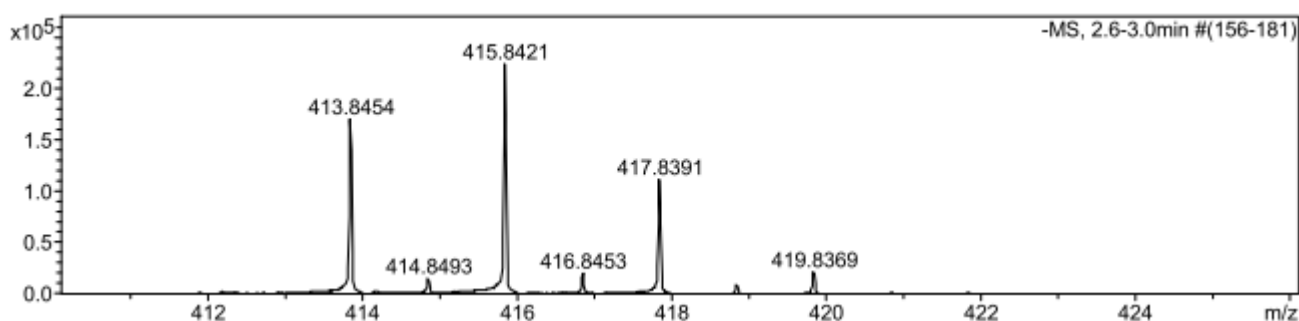
In conclusion, we synthesized mono(aryloxy)pentachlorocyclotriphosphazene **3** by aryloxylation of HCCP (1) with 3 equiv. of LiOAr in THF at -40 °C, and multi-substituted products were not obtained.<sup>11</sup> In mass experiment, chlorocyclotriphosphazenes  $\text{N}_3\text{P}_3\text{Cl}_n\text{R}_{6-n}$  would be partially hydrolyzed to give very small amount of  $\text{N}_3\text{P}_3\text{Cl}_{n-1}(\text{OH})\text{R}_{6-n}$ , which could not be detected by <sup>31</sup>P NMR and EI-MS. However, in ESI-MS, as  $\text{N}_3\text{P}_3\text{Cl}_{n-1}(\text{OH})\text{R}_{6-n}$  is easily ionized by deprotonation, whereas  $\text{N}_3\text{P}_3\text{Cl}_n\text{R}_{6-n}$  is hardly ionized. As the result, only  $\text{N}_3\text{P}_3\text{Cl}_{n-1}(\text{O}^-)\text{R}_{6-n}$  was detected. Though ESI-MS is very soft ionization method and detects parent peak, sometimes it detects most easily ionized species if it is very minor product, which is very misunderstanding.

Table 5. Mass spectra of chlorinated cyclotriphosphazene derivatives

	EI	ESI (negative)
$N_3P_3Cl_6$ ( <b>1</b> )	344.7443, 346.7380 348.7272, 350.7221 (Calcd for $Cl_6N_3P_3$ : 344.7436)	325.7707, 327.7677 329.7648, 331.7620 (Calcd for $Cl_5N_3OP_3$ : 325.7697)
$N_3P_3Cl_5(OC_6H_4OMe-4)$ ( <b>3a</b> )	432.8181, 434.8166 436.8069, 438.8060 (Calcd for $C_7H_7Cl_5N_3O_2P_3$ : 432.8195)	413.8454, 415.8421, 417.8391, 419.8369 (Calcd for $C_7H_7Cl_4N_3O_3P_3$ : 413.8454)
$N_3P_3Cl_5(OC_6H_4OCH_2CH_2OMe-4)$ ( <b>3b</b> )	476.8446, 478.8408 480.8412, 482.8395 (Calcd for $C_9H_{11}Cl_5N_3O_3P_3$ : 476.8456)	457.8713, 459.8692 461.8654, 463.8630 (Calcd for $C_9H_{11}Cl_4N_3O_4P_3$ : 457.8717)
$N_3P_3Cl_5(OC_6H_4Me-4)$ ( <b>3c</b> )	416.8180, 418.8144 420.8115, 422.8050 (Calcd for $C_7H_7Cl_5N_3OP_3$ : 416.8245)	397.8510, 399.8485 401.8456, 403.8426 (Calcd for $C_7H_7Cl_4N_3O_2P_3$ : 397.8505)
$N_3P_3Cl_5(OC_6H_4F-4)$ ( <b>3d</b> )	420.7972, 422.7923 424.7920, 426.7881 (Calcd for $C_6H_4Cl_5FN_3OP_3$ : 420.7994)	401.8265, 403.8236 405.8208, 407.8185 (Calcd for $C_6H_4Cl_4FN_3O_2P_3$ : 401.8254)
$N_3P_3Cl_5(OC_6H_4Cl-4)$ ( <b>3e</b> )	436.7727, 438.7674 440.7624, 442.7576 (Calcd for $C_6H_4Cl_6N_3OP_3$ : 436.7698)	417.7959, 419.7928 421.7898, 423.7871 (Calcd for $C_6H_4Cl_5N_3O_2P_3$ : 417.7959)
$N_3P_3Cl_5(OC_6H_4NO_2-4)$ ( <b>3f</b> )	447.7932, 449.7867 451.7846, 453.7869 (Calcd for $C_6H_4Cl_5N_4O_3P_3$ : 447.7939)	428.8242, 430.8159 432.8128, 434.8113 (Calcd for $C_6H_4Cl_4N_4O_4P_3$ : 428.8200)

(a) EI Ms of **3a**

	Observed m/z	Int%	Err [ppm / mmu]	U.S.	Composition
1	432.8181	44.67	-3.0 / -1.3	8.0	$C_7H_7Cl_5N_3O_2P_3$
2			+40.0 / +17.3	9.0	$C_7H_5Cl_5N_3O_2P_3$
3			+83.0 / +35.9	10.0	$C_7H_3Cl_5N_3O_2P_3$

(b) ESI Ms of **3a**Figure 3. MS of **3a****EXPERIMENTAL**

HCCP was a gift from Otsuka Chemical Company, Co. Ltd. ArOH (Tokyo Chemical Industry Co., Ltd.), *n*-BuLi (1.57 M in hexane, Kanto Chemical Co., Ltd.), and THF (dehydrated, Kanto Chemical Co., Ltd) were purchased and used without further purification.  $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{31}\text{P}$  NMR spectra were recorded on JEOL ECS-400 ( $^1\text{H}$ : 400 MHz,  $^{13}\text{C}$ : 100 MHz,  $^{31}\text{P}$ : 162 MHz). ESI Mass spectra and EI mass spectra were measured on Bruker Daltonics, micrOTOF II and Agilent Technologies, 6520 Accurate-Mass Q-TOF, respectively.

$\text{N}_3\text{P}_3\text{Cl}_5(\text{OC}_6\text{H}_4\text{-OMe-}p)$  (**3a**) was prepared as follows. A mixture of *p*-methoxyphenol (**2a**, 0.18 g, 1.5 mmol), *n*-BuLi (1.57 M, 1.0 mL, 1.57 mmol), and THF (5 mL) was stirred at  $-40\text{ }^\circ\text{C}$  for 1 h under argon atmosphere. To the reaction mixture was added HCCP (0.18 g, 0.52 mmol), and the whole mixture was stirred at  $-40\text{ }^\circ\text{C}$  for 3 h. To the reaction mixture was added sat. aq.  $\text{NH}_4\text{Cl}$  (10 mL), and the mixture was extracted with AcOEt (20 mL  $\times$  3). The combined organic layer was dried over anhydrous  $\text{Na}_2\text{SO}_4$ , filtered, and concentrated under reduced pressure. The resulting mixture was analyzed by  $^{31}\text{P}$  NMR to find that mono-substituted product (**3a**) was obtained as a sole product. The reaction mixture was purified by silica gel column chromatography to give pure **3a** in 91% yield.

Other  $\text{N}_3\text{P}_3\text{Cl}_5(\text{OAr})$  were also similarly synthesized.  $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{31}\text{P}$  NMR data were listed below. MS spectra were given in Table 5.

$\text{N}_3\text{P}_3\text{Cl}_6$  (**1**)  $^{31}\text{P}$  NMR  $\delta$  20.61 (s, 3P).

$\text{N}_3\text{P}_3\text{Cl}_5(\text{OC}_6\text{H}_4\text{OMe-}4)$  (**3a**)  $^1\text{H}$  NMR  $\delta$  6.86-6.90 (m, 2H), 7.14-7.20 (m, 2H);  $^{13}\text{C}$  NMR  $\delta$  55.72, 114.89, 122.34, 142.80, 157.99;  $^{31}\text{P}$  NMR  $\delta$  13.61 (t,  $J = 58.2$  Hz, 1P), 23.03 (d,  $J = 58.2$  Hz, 2P).

$\text{N}_3\text{P}_3\text{Cl}_5(\text{OC}_6\text{H}_4\text{OCH}_2\text{CH}_2\text{OMe-}4)$  (**3b**)  $^1\text{H}$  NMR  $\delta$  3.43 (s, 3H), 3.73 (t,  $J = 4.6$  Hz, 2H), 4.08 (t,  $J = 4.6$  Hz, 2H), 6.89-6.92 (m, 2H), 7.14-7.17 (m, 2H);  $^{13}\text{C}$  NMR  $\delta$  59.25 (s), 67.70 (s), 70.89 (s), 115.50 (s), 122.23 (d,  $J = 5.8$  Hz), 142.85 (d,  $J = 10.5$  Hz), 157.12 (s);  $^{31}\text{P}$  NMR  $\delta$  13.61 (t,  $J = 58.2$  Hz, 1P), 23.03 (d,  $J = 58.2$  Hz, 2P).

$\text{N}_3\text{P}_3\text{Cl}_5(\text{OC}_6\text{H}_4\text{Me-4})$  (**3c**)  $^1\text{H}$  NMR  $\delta$  2.34 (s, 3H), 7.11-7.14 (m, 2H), 7.16-7.20 (m, 2H);  $^{13}\text{C}$  NMR  $\delta$  20.97, 121.06, 130.50, 136.62, 147.23;  $^{31}\text{P}$  NMR  $\delta$  13.08 (t,  $J = 60.7$  Hz, 1P), 23.15 (d,  $J = 60.7$  Hz, 2P).

$\text{N}_3\text{P}_3\text{Cl}_5(\text{OC}_6\text{H}_4\text{F-4})$  (**3d**)  $^1\text{H}$  NMR  $\delta$  7.03-7.11 (m, 2H), 7.20-7.27 (m, 2H);  $^{13}\text{C}$  NMR  $\delta$  116.76 (d,  $J = 24.0$  Hz), 122.96 (m), 145.08 (d,  $J = 9.6$  Hz), 160.82 (d,  $J = 246.3$  Hz);  $^{31}\text{P}$  NMR  $\delta$  13.59 (t,  $J = 60.7$  Hz, 1P), 23.34 (d,  $J = 60.7$  Hz, 2P).

$\text{N}_3\text{P}_3\text{Cl}_5(\text{OC}_6\text{H}_4\text{Cl-4})$  (**3e**)  $^1\text{H}$  NMR  $\delta$  7.18-7.22 (m, 2H), 7.33-7.38 (m, 2H);  $^{13}\text{C}$  NMR  $\delta$  122.83 (d,  $J = 4.8$  Hz), 130.15 (s), 132.48 (d,  $J = 2.9$  Hz), 147.77 (d,  $J = 10.5$  Hz);  $^{31}\text{P}$  NMR  $\delta$  13.16 (t,  $J = 60.7$  Hz, 1P), 23.27 (d,  $J = 60.7$  Hz, 2P).

$\text{N}_3\text{P}_3\text{Cl}_5(\text{OC}_6\text{H}_4\text{NO}_2\text{-4})$  (**3f**)  $^1\text{H}$  NMR  $\delta$  7.43-7.46 (m, 2H), 8.30-8.32 (m, 2H);  $^{13}\text{C}$  NMR  $\delta$  122.37 (d,  $J = 5.8$  Hz), 125.88 (s), 146.07 (s), 153.59 (s);  $^{31}\text{P}$  NMR  $\delta$  12.41 (t,  $J = 63.2$  Hz, 1P), 23.26 (d,  $J = 63.2$  Hz, 2P).

$\text{N}_3\text{P}_3\text{Cl}_4(\text{OC}_6\text{H}_4\text{OMe-4})_2$  (**4a**) *trans*-isomer:  $^{31}\text{P}$  NMR  $\delta$  16.15 (d,  $J = 64.4$  Hz, 2P), 25.43 (t,  $J = 64.4$  Hz, 1P); *cis*-isomer  $^{31}\text{P}$  NMR  $\delta$  16.11 (d,  $J = 65.6$  Hz, 2P), 25.03 (t,  $J = 65.6$  Hz, 1P).

$\text{N}_3\text{P}_3\text{Cl}_3(\text{OC}_6\text{H}_4\text{OMe-4})_3$  (**5a**)  $\delta$  19.04 (s, 3P)

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7. We wondered why only one  $\text{ArO}^-$  was introduced in the presence of excess amount  $\text{ArOLi}$ : if solubility of  $\text{ArOLi}$  would not be high enough, the effective concentration of  $\text{ArOLi}$  might be much smaller than expected. It is worthy to note that the isolated **3a** did not give **4a** and/or **5a** even after treatment with an excess amount of **2a**/*n*-BuLi. Therefore, though it is not clear yet,  $\text{ArO}^-$  group would deactivate the remaining Cl-P bonds.<sup>8</sup>
8. Charge density of HCCP and mono-substituted  $\text{N}_3\text{P}_3\text{Cl}_5(\text{OPh})$  was calculated by Gaussian 09W (DFT,

B3LYP, 6-31G). From this results, P (PCl(OAr)) in  $N_3P_3Cl_5(OPh)$  seems to be more reactive than  $PCl_2$  in HCCP because O is more electron-negative than Cl. Therefore, charge density could not explain why second ArOLi could not be introduced and *non-gem*-substituted products were obtained with NaOPh. Since **3a-3f** are liquid, we can not analyze their structure by X-ray analysis.

9. A mixture of 4-methoxyphenol (**2a**, 10 mmol), LiOH·H<sub>2</sub>O (10.1 mmol), and H<sub>2</sub>O (25 mL) was stirred at room temperature for 30 min, and poured into toluene (100 mL). The mixture was distilled under 1 atm to remove H<sub>2</sub>O by azeotrope, and the residue was dried under reduce pressure to obtain lithium 4-methoxyphenoxide.
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