Selective substitution reaction of hexachlorocyclotriphosphazene (HCCP) with phenoxide

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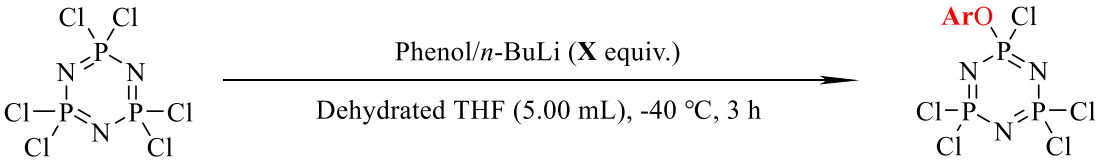
Hexachlorocyclotriphosphazene ($N_3P_3Cl_6$, HCCP, **1**) has a six-membered ring (N_3P_3) and six Cl atoms on the P atoms. These P-Cl bonds are active for nucleophilic substitution, and several nucleophiles are easily introduced. Usually, six same nucleophiles have been introduced to give $N_3P_3Nu^1{}_6$. If partial nucleophilic substitution can be performed selectively, more than two kinds of nucleophiles can be introduced to give multi-functionalized materials ($N_3P_3Nu^1{}_xNu^2{}_{(6-x)}$, etc). When HCCP was allowed to react with ArONa in THF, though partial nucleophilic substitution occurred, product selectivity was not high enough; a complex mixture of mono- (**2**), di-, tri-, tetra-, penta-, and hexasubstituted products was obtained.[1] On the other hand, we found ArOLi/THF gave only mono-substituted product **2** even when an excess amount of ArOLi was used.



1 (0.5 mmol) **2**

Figure 1. Effect of equiv. of *p*-methoxyphenol/*n*-BuLi.

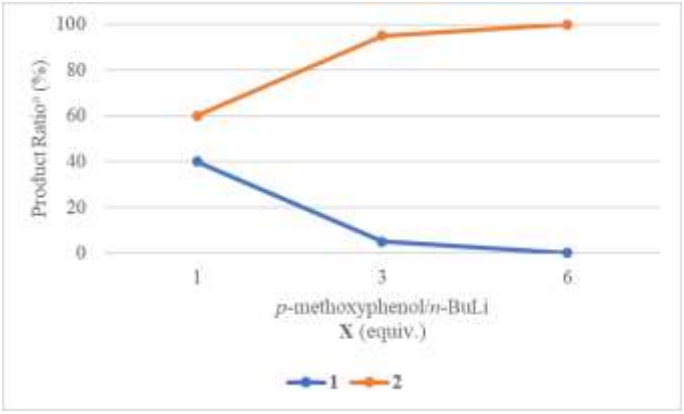


Table 1. Reaction **1** with phenol/*n*-BuLi.

Phenol (10 equiv.)	Product Ratio[a] (%)	
	1	**2**
p-methyl	34	66
p-chloro	13	87
p-fluoro	16	84
p-methoxy	9	91

[a] Determined by ^{31}P NMR of the reaction mixture.

HCCP was allowed to react with *p*-methoxyphenol/*n*-BuLi (1/1 equiv.) in THF at -40 ºC for 3 h to give **2a** (Ar = $MeOC_6H_4$) in 60% yield. When 6 equiv. of *p*-methoxyphenol/*n*-BuLi was used, **2a** was obtained in almost 100% yield, and no multi-substituted products were detected (Figure 1). Other phenols such as *p*-methyl, *p*-chloro, and *p*-fluoro phenols gave similar mono-phenoxylated triphosphazene in 66, 87, 84%, respectively (Table 1).

1) Y. W. Chen-Yang.; S. J. Chen.; B.D. Tsai. *Ind. Eng. Chem. Res.* **1991**, 30, 1314-1319.