

# Arylation Reaction of *N*-Dichlorophosphoryl-*P*-trichlorophosphazene

M. Arslan,<sup>1</sup> F. Aslan,<sup>2</sup> and A. I. Ozturk<sup>2</sup>

<sup>1</sup>Chemistry Department, Firat University, TR-23169 Elazig, Turkey

<sup>2</sup>Chemistry Department, Harran University, TR-63100 Sanliurfa, Turkey

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**ABSTRACT:** The reactions of *N*-dichlorophosphoryl-*P*-trichlorophosphazene ( $\text{Cl}_3\text{P}=\text{N}-\text{POCl}_2$ ) with phenylmagnesium chloride, *o*-tolylmagnesium chloride, *p*-tolylmagnesium chloride, *p*-chlorophenylmagnesium chloride, 2-mesitylmagnesium bromide, and 2-thienyl lithium were studied. The resulting pentaaryl phosphazenes  $\text{R}_5\text{P}=\text{N}-\text{P}(\text{O})\text{R}_2$  were separated by using column chromatography, their structures were defined by IR, elemental analysis,  $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{31}\text{P}$  NMR, and mass spectroscopy. © 2003 Wiley Periodicals, Inc. Heteroatom Chem 14:138–143, 2003; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.10114

## INTRODUCTION

Only a few short-chain phosphazenes have been characterized in detail [1–9]. The reactions of compound **1** with amines and alcohols have been reviewed [10,11]. The structures of **1** [12] and some of its derivatives, such as its pentaamide derivative  $(\text{PhNH})_3\text{P}=\text{N}-\text{P}(\text{O})(\text{NHPh})_2$  [13], its geminal-bis(diisopyropylamino) derivative  $\text{Cl}[\text{NCH}(\text{CH}_3)_2]_2\text{P}=\text{N}-\text{P}(\text{O})\text{Cl}_2$  [14], and its geminal-bis(2,4,6-*tert*-butylphenoxy)  $\text{Cl}(\text{OC}_6\text{H}_2\text{Bu}'-2,4,6)_2\text{P}=\text{N}-\text{P}(\text{O})\text{Cl}_2$  and bis(2,6-di-*tert*-butyl-4-methylphenoxy)  $\text{Cl}(\text{OC}_6\text{H}_2\text{Bu}'-2,6-\text{Me}-4)_2\text{P}=\text{N}-\text{P}(\text{O})\text{Cl}_2$

derivatives [15] have been reported. These molecules can be used as structural models for the inorganic polymers with a large range of properties [2,16] and applications [17–24].

Three routes can accomplish the synthesis of phosphazenes that contain alkyl or aryl groups bonded directly to phosphorus by direct synthesis, Friedel–Craft reactions, and the interaction of organometallic compounds with halophosphazenes [1]. The reactions between halogenophosphazenes and main group organometallic reagents have been studied during last 30 years [2,25], but these reactions can be complex, and some of the earlier work in this area has had to be reinterpreted as the degree of complexity has been recognized [26]. Several transition-metal-containing cyclic phosphazenes have been synthesized [27]. In the synthesis of alkyl- and aryl-substituted phosphazenes, a halophosphazene is reacted with an organolithium or Grignard reagent [28–33]. Although there are many publications about cyclic, polymeric alkyl- or arylphosphazenes [34–40], the synthesis of linear alkyl-substituted phosphazenes has been performed with only limited success [41,42].

Here we report the reactions of  $\text{Cl}_3\text{P}=\text{N}-\text{P}(\text{O})\text{Cl}_2$  (**1**) with aryllithium and aryl-Grignard reagents. Pentasubstituted phosphazenes were obtained as major products.

## RESULTS AND DISCUSSION

The reaction of **1** with 10 equiv. of phenylmagnesium chloride, *o*-tolylmagnesium chloride, *p*-tolylmagnesium chloride, *p*-chlorophenylmagnesium

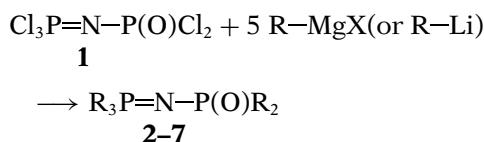
Correspondence to: M. Arslan; e-mail: marslan07@yahoo.com.

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chloride, 2-mesylmagnesium bromide, and 2-thienyl lithium in toluene gave the pentasubstituted compounds as the main products.



They were isolated from the reaction mixture by column chromatography and characterized by elemental analysis,  $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{31}\text{P}$  NMR, mass spectrometry, and FT-IR. The solvents used for the purification of the compounds could not be removed completely as observed by  $^1\text{H}$ ,  $^{13}\text{C}$  NMR spectra. Thus the presence of these trace amounts of solvent affect the elemental analysis, in particular the carbon value. The physical properties, molecular weights, and analytical data are given in Table 1. (Structures of **2-7** are shown in Scheme 1.)

In the reactions of halophosphazene with organolithium or Grignard reagents, P=N bond cleavage can compete with halogen replacement [43]. The ring-opened process can be observed in cyclophosphazenes [1]. Thus, phosphazene degradation accompanies substitution. This decreases the yields of final products. From hexachlorocyclotriphosphazatriene and methylolithium, for example, ring-opened phosphazenes and small amounts of monomethyl and dimethyl chlorocyclotriphosphazatriene were obtained [38]. The nature of solvent and

of the reagents may also affect the yield. In addition, the steric hindrance plays an important role in such reactions. In the reaction of *m*-, *p*-, and *o*-tolylmagnesium bromide with chlorophosphazenes, the nucleophilic attack of the *m*-isomer appears to be more difficult and essentially lacks with the *o*-isomer [42]. In our study, the pentasubstituted phosphazene is obtained in 10% yield from the reaction with *o*-tolylmagnesium chloride. 2-Mesylmagnesium bromide gives the lowest yield because of the high steric hindrance.

The characteristic stretching peaks in the IR spectra of the phosphazenes have been assigned as in Table 2. The P=N and P=O stretching vibrations, 1180–1330 and 1160–1230  $\text{cm}^{-1}$  respectively, are characteristic of phosphazenes. Compared to **1** these peaks are shifted to longer wavelengths for **2-7**.

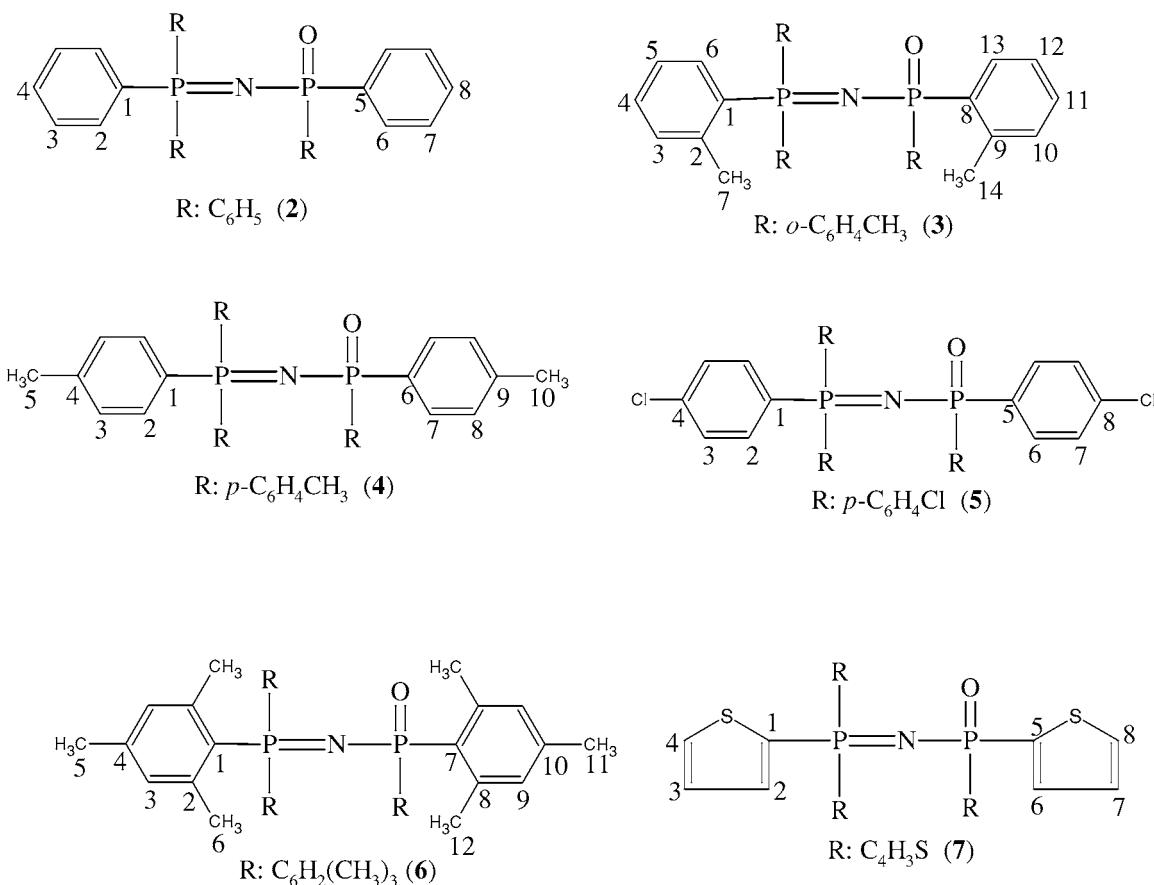
The NMR data of **1-7** are presented in Table 3–5. The AB spin pattern in the  $^{31}\text{P}$  NMR spectra indicate that the phosphazene skeleton is intact. While phosphorus signals of **1** are observed at the high field, the signals of the aryl-substituted phosphazenes move to the lower field (Table 3). The 2-thienyl-substituted phosphazene (**7**) shows the least difference from **1**.

In the  $^1\text{H}$  NMR spectra of the aryl-substituted phosphazenes (**2-7**), the protons in the phosphoryl ( $-\text{P}(\text{O})\text{Ar}_2$ ) and in the phosphazene ( $\text{Ar}_3\text{P}=\text{N}-$ ) moiety can be distinguished in some cases, the latter being more shielded than the former. The 2:3 ratio of integral intensities for the two sets of protons is observed. There are also two sets of carbon atoms

TABLE 1 Physical Properties, Molecular Weight, and Analytical Data of **1-7**

Compound	R	m.p. ( $^{\circ}\text{C}$ )	Yield (%)	Mol. Weight <sup>a</sup>		Calcd	Found	
				Calcd	Found			
<b>1</b>	Cl	32	51	269.5	—	—	—	
<b>2</b>	$\text{C}_6\text{H}_5$	151	35	477	476 ( $\text{M}-1$ ) 183 ( $\text{C}_{12}\text{H}_8\text{P}^+$ ) 151 ( $\text{C}_{12}\text{H}_7^+$ )	C H N C H N	76.46 5.28 2.93 76.77 6.44 2.56	75.31 5.25 2.85 75.78 6.85 2.80
<b>3</b>	<i>o</i> - $\text{C}_6\text{H}_4\text{CH}_3$	145	10	547	—	C H N C H N	76.77 6.44 2.56 75.61 6.32 2.43	
<b>4</b>	<i>p</i> - $\text{C}_6\text{H}_4\text{CH}_3$	181	15	547	547 90 ( $\text{C}_7\text{H}_6^+$ ) 92 ( $\text{C}_7\text{H}_8^+$ )	C H N	76.77 6.44 2.56	
<b>5</b>	<i>p</i> - $\text{C}_6\text{H}_4\text{Cl}$	142	20	647	647 75 ( $\text{C}_6\text{H}_3^+$ ) 47 ( $\text{CCl}^+$ )	C H N	55.46 3.10 2.16	
<b>6</b>	$\text{C}_6\text{H}_2(\text{CH}_3)_3$	201	6	687	688 ( $\text{M}+1$ ) $\text{M}-105$ 91 ( $\text{C}_7\text{H}_7^+$ )	C H N	78.60 8.01 2.04	
<b>7</b>	$\text{C}_4\text{H}_3\text{S}$	173	15	507	507 38 ( $\text{C}_3\text{H}_2^+$ ) 44 ( $\text{CS}^+$ )	C H N	47.32 2.98 2.76	
							46.44 2.52 2.59	

<sup>a</sup>Molecular weight and only the first two peaks of MS in the relative abundance order are shown.



SCHEME 1 The structures of the compounds 2–7.

with the same ratio between the integral intensities of the signals of similar carbons. This observation indicates that aryl groups have replaced all chlorine atoms in **1**.

The protons next to the phosphorus atoms are very well characterized by the  $^1\text{H}$  NMR spectra that show peaks at the lowest down field of the aromatic protons (Table 4). The methyl protons of **3**, **4**, and **6** give singlets at  $\delta = 2.05$  and  $2.13$ ,  $\delta = 2.20$  and  $2.28$ , and  $\delta = 2.10$ ,  $2.18$ ,  $2.20$ ,  $2.28$ , respectively. The phenyl protons are observed at  $\delta = 7.63$ – $7.70$ ,

$\delta = 7.63$ – $7.72$ ,  $\delta = 7.51$ – $7.57$ ,  $\delta = 7.63$ – $7.68$  as doublets at the lower downfield for compounds **2**, **3**, **4**, and **5**, respectively. While the aromatic protons appear at  $\delta = 6.50$ – $6.65$  for **6**, four protons are shown as two doublets at  $\delta = 7.45$ – $7.48$  and  $\delta = 7.73$ – $7.77$  for **7**.

In the  $^{13}\text{C}$  NMR spectra (Table 5), the carbon atoms attached directly to phosphorus atoms are generally observed at lowest field and with the largest  $J_{\text{PC}}$  values. *Ips*o carbon atoms in the  $-\text{POAr}_2$  moiety are shielded more than in the  $-\text{PNAr}_3$  moiety.

TABLE 2 Characteristic IR Vibrations (in  $\text{cm}^{-1}$ ) of 1–7

Compound	$\nu_{\text{C}-\text{H ar.}}$	$\nu_{\text{C}-\text{H al.}}$	$\nu_{\text{P}=\text{N}}$	$\nu_{\text{P}=\text{O}}$	$\nu_{\text{P}-\text{N}}$	$\nu_{\text{P}-\text{Cl}}$
<b>1</b>	–	–	1338	1263	770	650
<b>2</b>	3021–3075	–	1265	1174	748	–
<b>3</b>	3005–3051	2859–2967	1211	1192	760	–
<b>4</b>	3019–3071	2866–2975	1234	1168	761	–
<b>5</b>	3014–3079	2852–2956	1241	1170	742	–
<b>6</b>	3024	2851–2953	1194	1180	754	–
<b>7</b>	3097	3054–3075	1247	1180	746	–

TABLE 3  $^{31}\text{P}$  NMR Data of 1–7

Compound	$\delta_{\text{PN}}$	$\delta_{\text{PO}}$	$J_{\text{PNP}}$
<b>1</b>	–2.6	–10.6	21.3
<b>2</b>	15.5	14.4	ND
<b>3</b>	14.8	14.6	ND
<b>4</b>	15.4	13.8	ND
<b>5</b>	14.7	14.2	ND
<b>6</b>	24.9	20.2	1.93
<b>7</b>	0.60	–10.3	8.10

ND: Not determined.

TABLE 4  $^1\text{H}$  NMR Data of 2–7

<b>2</b>	7.19 ( $\text{H}^8$ , $\text{H}^7$ , $^5\text{J}_{\text{P}CCCC\text{H}}$ : 1.9), 7.30 ( $\text{H}^3$ , $^4\text{J}_{\text{P}CCCC\text{H}}$ : 4.7), 7.41 ( $\text{H}^4$ , $^4\text{J}_{\text{P}CCCC\text{H}}$ : 6.0), 7.63 ( $\text{H}^2$ , $^3\text{J}_{\text{P}CC\text{H}}$ : 7.2), 7.70 ( $\text{H}^6$ , $^3\text{J}_{\text{P}CC\text{H}}$ : 6.6) ( $\text{H}^7$ : $\text{H}^3$ : $\text{H}^4$ : $\text{H}^2$ : $\text{H}^6$ = 3.50:3.45:1.70:3.40:1.92)
<b>3</b>	2.05 ( $\text{H}^7$ ), 2.13 ( $\text{H}^{14}$ ), 7.72 ( $\text{H}^{13}$ , $^3\text{J}_{\text{P}CC\text{H}}$ : 7.4), 7.63 ( $\text{H}^6$ , $^3\text{J}_{\text{P}CC\text{H}}$ : 7.8), 7.33 ( $\text{H}^5$ , $^4\text{J}_{\text{P}CCCC\text{H}}$ : 6.1), 7.13 ( $\text{H}^{12}$ and $\text{H}^{10}$ , $^4\text{J}_{\text{P}CCCC\text{H}}$ : 7.4), 7.08 ( $\text{H}^4$ , $^5\text{J}_{\text{P}CCCC\text{H}}$ : 7.3), 6.98 ( $\text{H}^3$ , $^4\text{J}_{\text{P}CCCC\text{H}}$ : 7.4), 6.90 ( $\text{H}^{11}$ , $^5\text{J}_{\text{P}CCCC\text{H}}$ : 4.5) ( $\text{H}^7$ : $\text{H}^{14}$ : $\text{H}^{11}$ : $\text{H}^3$ : $\text{H}^{13}$ : $\text{H}^6$ : $\text{H}^5$ : $\text{H}^{12,10}$ : $\text{H}^4$ = 3.6:2.4:0.8:1.2:0.7:1.2:1.2:1.8:1.2)
<b>4</b>	2.20 ( $\text{H}^{10}$ ), 2.28 ( $\text{H}^5$ ), 6.95 ( $\text{H}^8$ , $^4\text{J}_{\text{P}CCCC\text{H}}$ : 5.5), 7.10 ( $\text{H}^3$ , $^4\text{J}_{\text{P}CCCC\text{H}}$ : 5.5), 7.51 ( $\text{H}^2$ , $^3\text{J}_{\text{P}CC\text{H}}$ : 8.1), 7.57 ( $\text{H}^7$ , $^3\text{J}_{\text{P}CC\text{H}}$ : 7.9) ( $\text{H}^5$ : $\text{H}^{10}$ : $\text{H}^3$ : $\text{H}^8$ : $\text{H}^2$ : $\text{H}^7$ = 5.4:3.4:3.2:2.1:3.2:2.1)
<b>5</b>	7.26 ( $\text{H}^7$ , $^4\text{J}_{\text{P}CCCC\text{H}}$ : 6.3), 7.43 ( $\text{H}^3$ , $^4\text{J}_{\text{P}CCCC\text{H}}$ : 6.1), 7.63 ( $\text{H}^2$ , $^3\text{J}_{\text{P}CC\text{H}}$ : 8.5), 7.68 ( $\text{H}^6$ , $^3\text{J}_{\text{P}CC\text{H}}$ : 9.0) ( $\text{H}^7$ : $\text{H}^3$ : $\text{H}^2$ : $\text{H}^6$ = 3.6:5.8:5.5:3.5)
<b>6</b>	2.10 ( $\text{H}^5$ ), 2.18 ( $\text{H}^{11}$ ), 2.20 ( $\text{H}^{12}$ ), 2.28 ( $\text{H}^6$ ), 6.50 and 6.65 ( $\text{H}^3$ and $\text{H}^9$ , $^4\text{J}_{\text{P}CCCC\text{H}}$ : 3.6) ( $\text{H}^{13,9}$ : $\text{H}^6$ : $\text{H}^{12}$ : $\text{H}^{11}$ : $\text{H}^5$ = 1.8:3.1:2.1:1.1:1.6)
<b>7</b>	6.98 ( $\text{H}^7$ , $^4\text{J}_{\text{P}CCCC\text{H}}$ : 1.8), 7.15 ( $\text{H}^3$ , $^4\text{J}_{\text{P}CCCC\text{H}}$ : 2.1), 7.45 ( $\text{H}^6$ , $^3\text{J}_{\text{P}CC\text{H}}$ : 4.3), 7.48 ( $\text{H}^8$ , $^4\text{J}_{\text{P}CSCH}$ : 4.3), 7.73 ( $\text{H}^2$ , $^3\text{J}_{\text{P}CC\text{H}}$ : 5.1), 7.77 ( $\text{H}^4$ , $^4\text{J}_{\text{P}CSCH}$ : 5.1) ( $\text{H}^7$ : $\text{H}^3$ : $\text{H}^6$ : $\text{H}^8$ : $\text{H}^2$ : $\text{H}^4$ = 2.8:4.2:2.8:2.8:4.3:4.3)

For numbering see Scheme 1; coupling constants  $J$  (Hz).

The electron impact MS of **4**, **5**, and **7** showed the well-defined molecular ions at  $m/z$  547 (6%), 647 (4%), and 507 (1%), respectively. The parent ion peaks are observed at  $m/z$  476 (15%) as  $\text{M} - 1$  for **2** and at 688 (1%) as  $\text{M} + 1$  for **6**. The peaks at  $m/z$  values of 76 (dominant ion,  $\text{C}_6\text{H}_4^+$ , 100%), 399, 401, 321, 183, and 151 correspond to the loss of  $\text{C}_6\text{H}_5$ ,  $\text{C}_{12}\text{H}_8\text{P}$  groups for **2**. The dominant ion peaks at  $m/z$  90 ( $\text{C}_7\text{H}_6^+$ , 100%), 75 ( $\text{C}_6\text{H}_3^+$ , 100%), 582 ( $\text{M} - 105$ ,  $\text{C}_8\text{H}_9^+$ , 100%), 38 ( $\text{C}_3\text{H}_2^+$ , 100%) for **4**, **5**, **6**, and **7**, respectively.

## CONCLUSION

Pentaaryl-substituted phosphazenes were isolated from the nucleophilic substitution of *N*-dichlorophosphoryl-*P*-trichlorophosphazene by phenylmagnesium chloride, *o*-tolylmagnesium chloride, *p*-tolylmagnesium chloride, *p*-chlorophenylmagnesium chloride, 2-mesitylmagnesium bromide, 2-thienyl lithium. The products were defined as diphenylphosphinyl-triphenylphosphazene, bis(*o*-tolyl)phosphinyl-tris(*o*-tolyl)phosphazene, bis(*p*-tolyl)phosphinyl-tris(*p*-tolyl)phosphazene, bis(*p*-chlorophenyl)phosphinyl-tris(*p*-chlorophenyl)phosphazene, bis(2-mesityl)phosphinyl-tris(2-mesityl)phosphazene, and bis(2-thienyl)phosphinyl-tris(2-thienyl)phosphazene.

TABLE 5  $^{13}\text{C}$  NMR Data of 2–7

<b>2</b>	128.0 ( $\text{C}^6$ , $^2\text{J}_{\text{PCC}}$ : 12.6), 128.9 ( $\text{C}^2$ , $^2\text{J}_{\text{PCC}}$ : 12.8), 131.6 ( $\text{C}^7$ , $^3\text{J}_{\text{PCCC}}$ : 9.8), 133.0 ( $\text{C}^3$ , $^3\text{J}_{\text{PCCC}}$ : 11.1), 130.0 ( $\text{C}^8$ , $^4\text{J}_{\text{PCCCC}}$ : 2.4), 132.5 ( $\text{C}^4$ , $^4\text{J}_{\text{PCCCC}}$ : 2.8), 130.5 ( $\text{C}^5$ , $^1\text{J}_{\text{PC}}$ : 52.2), 139.0 ( $\text{C}^1$ , $^1\text{J}_{\text{PC}}$ : 173.2)
<b>3</b>	21.8 ( $\text{C}^{14}$ , $^3\text{J}_{\text{PCCC}}$ : 3.9), 22.8 ( $\text{C}^7$ , $^3\text{J}_{\text{PCCC}}$ : 4.4), 124.9 ( $\text{C}^{13}$ , $^2\text{J}_{\text{PCC}}$ : 12.2), 126.1 ( $\text{C}^6$ , $^2\text{J}_{\text{PCC}}$ : 13.3), 129.0 ( $\text{C}^8$ , $^1\text{J}_{\text{PC}}$ : 101.2), 130.2 ( $\text{C}^{11}$ , $^4\text{J}_{\text{PCCCC}}$ : 1.8), 131.2 ( $\text{C}^{10}$ , $^3\text{J}_{\text{PCC}}$ : 12.6), 132.3 ( $\text{C}^4$ , $^4\text{J}_{\text{PCCCC}}$ : 2.6), 132.6 ( $\text{C}^3$ , $^3\text{J}_{\text{PCCC}}$ : 8.8), 133.2 ( $\text{C}^{12}$ , $^3\text{J}_{\text{PCCC}}$ : 9.6), 134.8 ( $\text{C}^5$ , $^3\text{J}_{\text{PCCC}}$ : 13.5), 137.2 ( $\text{C}^1$ , $^1\text{J}_{\text{PC}}$ : 130.8), 141.5 ( $\text{C}^9$ , $^2\text{J}_{\text{PCC}}$ : 11.0), 142.9 ( $\text{C}^2$ , $^2\text{J}_{\text{PCC}}$ : 9.2)
<b>4</b>	21.8 ( $\text{C}^{10}$ ), 21.9 ( $\text{C}^5$ ), 128.3 ( $\text{C}^6$ , $^1\text{J}_{\text{PC}}$ : 111.8), 128.6 ( $\text{C}^7$ , $^2\text{J}_{\text{PCC}}$ : 12.8), 129.5 ( $\text{C}^2$ , $^2\text{J}_{\text{PCC}}$ : 13.4), 131.6 ( $\text{C}^8$ , $^3\text{J}_{\text{PCCC}}$ : 10.2), 133.0 ( $\text{C}^3$ , $^3\text{J}_{\text{PCCC}}$ : 11.5), 137.2 ( $\text{C}^1$ , $^1\text{J}_{\text{PC}}$ : 137.6), 139.7 ( $\text{C}^9$ , $^4\text{J}_{\text{PCCCC}}$ : 1.7), 142.5 ( $\text{C}^4$ , $^4\text{J}_{\text{PCCCC}}$ : 2.8)
<b>5</b>	128.3 ( $\text{C}^5$ , $^1\text{J}_{\text{PC}}$ : 108.0), 128.6 ( $\text{C}^6$ , $^2\text{J}_{\text{PCC}}$ : 13.3), 129.7 ( $\text{C}^2$ , $^2\text{J}_{\text{PCC}}$ : 13.6), 132.9 ( $\text{C}^7$ , $^3\text{J}_{\text{PCCC}}$ : 10.3), 134.1 ( $\text{C}^3$ , $^3\text{J}_{\text{PCCC}}$ : 12.3), 137.2 ( $\text{C}^1$ , $^1\text{J}_{\text{PC}}$ : 135.0), 137.0 ( $\text{C}^8$ , $^4\text{J}_{\text{PCCCC}}$ : 3.1), 139.9 ( $\text{C}^4$ , $^4\text{J}_{\text{PCCCC}}$ : 3.2)
<b>6</b>	21.2 ( $\text{C}^5$ and $\text{C}^{11}$ ), 23.0 ( $\text{C}^6$ , $^3\text{J}_{\text{PCCC}}$ : 3.7), 23.7 ( $\text{C}^{12}$ , $^3\text{J}_{\text{PCCC}}$ : 4.1), 128.5 ( $\text{C}^7$ , $^1\text{J}_{\text{PC}}$ : 112.1), 130.6 ( $\text{C}^3$ , $^3\text{J}_{\text{PCCC}}$ : 11.8), 131.7 ( $\text{C}^9$ , $^3\text{J}_{\text{PCCC}}$ : 11.2), 135.5 ( $\text{C}^1$ , $^1\text{J}_{\text{PC}}$ : 126.0), 138.5 ( $\text{C}^{10}$ , $^4\text{J}_{\text{PCCCC}}$ : 2.4), 140.7 ( $\text{C}^4$ , $^4\text{J}_{\text{PCCCC}}$ : 2.7), 141.6 ( $\text{C}^2$ and $\text{C}^8$ , $^2\text{J}_{\text{PCC}}$ : 10.7)
<b>7</b>	128.0 ( $\text{C}^6$ , $^2\text{J}_{\text{PCC}}$ : 15.7), 129.0 ( $\text{C}^2$ , $^2\text{J}_{\text{PCC}}$ : 16.0), 131.8 ( $\text{C}^7$ , $^3\text{J}_{\text{PCCC}}$ : 5.7), 133.3 ( $\text{C}^5$ , $^1\text{J}_{\text{PC}}$ : 132.8), 133.8 ( $\text{C}^8$ , $^3\text{J}_{\text{PCSC}}$ : 11.6), 135.2 ( $\text{C}^3$ , $^3\text{J}_{\text{PCCC}}$ : 5.9), 138.6 ( $\text{C}^4$ , $^3\text{J}_{\text{PCSC}}$ : 12.7), 142.0 ( $\text{C}^1$ , $^1\text{J}_{\text{PC}}$ : 190.5)

For numbering see Scheme 1; coupling constants  $J$  (Hz).

## EXPERIMENTAL SECTION

### General Remarks

Solvents and other liquids used in the experimental works were dried by conventional methods. All reactions were monitored by using Kieselgel 60 F254 (silica gel) precoated TLC plates and the separating conditions were determined. The separation of products was carried out by flash column chromatography, using Kieselgel 60 (60–230 mesh).

IR spectra were recorded with an ATI Unicam Mattson 1000 FTIR spectrophotometer.  $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{31}\text{P}$  NMR spectra were recorded using a Bruker DPX-400 High Performance Digital FT-NMR spectrometer operating at 400.13, 100.63, and 161.98 MHz, respectively. All data was recorded for solutions in  $\text{CDCl}_3$ . The  $^1\text{H}$  and  $^{13}\text{C}$  chemical shifts were measured using  $\text{SiMe}_4$  as an internal standard, the  $^{31}\text{P}$  chemical shifts, using 85%  $\text{H}_3\text{PO}_4$  as an external standard. Chemical shifts downfield from the standard are assigned positive  $\delta$  values. Electron impact mass spectra were obtained by Micromass UK Platform-II spectrometer. Microanalysis was carried out by LECO 932 CHNS-O apparatus. The starting material **1** was prepared by the method of Emsley,

Moore, and Udy and purified by vacuum distillation [44].

$(C_6H_5)_3P=N-P(O)(C_6H_5)_2$  (**2**). Phenylmagnesium chloride 13.5 ml, 2 M in THF was slowly added dropwise to **1** (1.46 g, 5.4 mmol) in 150 ml of benzene in the reaction vessel by stirring for 0.5 h at ambient temperature and was then refluxed for 24 h. After the reaction was complete, the precipitated salt ( $MgCl_2$ ) was filtered off and the solvent was removed under vacuum. The residue was examined by TLC, using chloroform/acetone (2:1),  $R_f$  value is 0.51. They were separated by using column chromatography. After the solvent was removed, a white solid formed in 35% yield, m.p. 151°C.

$(o-CH_3C_6H_4)_3P=N-P(O)(o-CH_3C_6H_4)_2$  (**3**). *o*-Tolylmagnesium chloride (22 ml, 1 M in THF) and **1** (1.18 g, 4.4 mmol in 150 ml of benzene) were used for the preparation of **3** as for **2**. The residue was chromatographed ( $R_f$  = 0.63, chloroform/acetone 4:1). Compound **3** was obtained in 10% yield, m.p. 145°C.

$(p-CH_3C_6H_4)_3P=N-P(O)(p-CH_3C_6H_4)_2$  (**4**). *p*-Tolylmagnesium chloride (27 ml, 1 M in ether) and **1** (1.45 g, 5.3 mmol in 150 ml of toluene) were used for the preparation of **4** as for **2**. The residue was chromatographed ( $R_f$  = 0.40, chloroform/acetone 3:1). Compound **4** was obtained in 15% yield, m.p. 181°C.

$(p-ClC_6H_4)_3P=N-P(O)(p-ClC_6H_4)_2$  (**5**). *p*-Chlorophenylmagnesium chloride (20.4 ml, 1 M in THF) and **1** (1.11 g, 4.1 mmol in 150 ml of toluene) were used for the preparation of **5** as for **2**. The residue was chromatographed ( $R_f$  = 0.55, chloroform/acetone 8:1). Compound **5** was obtained in 20% yield, m.p. 142°C.

$[(CH_3)_3C_6H_2]_3P=N-P(O)[(CH_3)_3C_6H_2]_2$  (**6**). 2-Mesitylmagnesium bromide (28 ml, 1 M in ether) and **1** (1.51 g, 5.6 mmol in 150 ml of toluene) were used for the preparation of **6** as for **2**. The residue was chromatographed ( $R_f$  = 0.55, chloroform/acetone 5:1). Compound **6** was obtained in 6% yield, m.p. 201°C.

$(C_4H_3S)_3P=N-P(O)(C_4H_3S)_2$  (**7**). 2-Thienyl lithium (28 ml, 1 M in THF) and **1** (1.51 g, 5.6 mmol in 150 ml of toluene) were used for the preparation of **7** as for **2**. The residue was chromatographed ( $R_f$  = 0.38, chloroform/acetone 2:1). Compound **7** was obtained in 15% yield, m.p. 173°C.

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