*Aust. J. Chem.* **2013**, *66*, 1155–1162 http://dx.doi.org/10.1071/CH13141

Full Paper

# Phosphenium-Insertion and Chloronium-Addition Reactions Involving the *cyclo*-Phosphanes $(t-BuP)_n$ (n = 3, 4)

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The transfer of a Ph<sub>2</sub>P<sup>+</sup>-moiety provided by Ph<sub>2</sub>PCl and chloronium-addition with PCl<sub>5</sub> or PhICl<sub>2</sub> to the *cyclo*-phosphanes (*t*-BuP)<sub>n</sub> (n = 3 (**4**), 4 (**5**)) were investigated. The reactions strongly depend on the presence of GaCl<sub>3</sub> or Me<sub>3</sub>SiOTf as a halide abstracting reagent. The reaction of **4** with Ph<sub>2</sub>PCl and GaCl<sub>3</sub> quantitatively yields cation [Ph<sub>2</sub>P(*t*-BuP)<sub>3</sub>]<sup>+</sup> (**6**<sup>+</sup>) as a GaCl<sub>4</sub><sup>-</sup>-salt. Using Me<sub>3</sub>SiOTf as a halide abstracting reagent leads to the ring expansion of (*t*-BuP)<sub>3</sub> (**4**) to tetrameric (*t*-BuP)<sub>4</sub> (**5**) and cation **6**<sup>+</sup> is only formed as a minor product. Chloronium addition employing the PCl<sub>5</sub>/GaCl<sub>3</sub> or PhICl<sub>2</sub>/Me<sub>3</sub>SiOTf systems as Cl<sup>+</sup>-sources to **4** gives complex reaction mixtures. In contrast, the Cl<sup>+</sup>-addition to **5** gives cation [Cl(*t*-BuP)<sub>4</sub>]<sup>+</sup> (**8**<sup>+</sup>) quantitatively when the system PCl<sub>5</sub>/GaCl<sub>3</sub> is used. Utilising PhICl<sub>2</sub> in the presence of Me<sub>3</sub>SiOTf gives *t*-BuPCl<sub>2</sub> as the main product.

Manuscript received: 29 March 2013. Manuscript accepted: 7 May 2013. Published online: 31 May 2013.

## Introduction

The systematic development of polyphosphorus cations is of considerable current interest in fundamental phosphorus chemistry.<sup>[1]</sup> Polyphosphorus cations feature structures based on cagelike,<sup>[2]</sup> cyclo-<sup>[3]</sup> or catena-phosphanylphosphonium<sup>[4]</sup> motifs. Salts of cyclo-phosphanylphosphonium ions are still rare and, therefore, novel synthetic procedures are desirable to expedite the development of the chemistry of this class of compounds. A variety of methods for their systematic synthesis are in place in which the most common procedures employ alkylation<sup>[3]</sup> or protonation<sup>[3d]</sup> protocols of cyclo-polyphosphanes. Insertion reactions of phosphenium ions into cyclo-polyphosphanes are also known and proceed either via a ring-expansion<sup>[5,3b,3c]</sup> or a redistribution process.<sup>[6,3c]</sup> Reductive coupling reactions are also reported in which the utilisation of chloro-substituted phosphanylphosphonium ions,<sup>[7]</sup> PCl<sub>3</sub>,<sup>[8]</sup> or secondary phosphanes<sup>[9]</sup> render versatile approaches for the generation of cyclic polyphosphorus cations. Only recently, halonium addition reactions to cyclo-polyphosphanes such as  $(CyP)_4(1)$  were reported which offer a versatile approach to halogen-substituted, *cyclo*-poly-phosphorus cations.<sup>[10]</sup> This was demonstrated by the reaction of 1 with PCl<sub>5</sub> as a chloronium ion source and GaCl<sub>3</sub> as a chloride abstracting reagent in various stoichiometries. This allowed for the stepwise preparation and isolation of cations  $2^+$  and  $3^{2+}$  as metallate salts (Scheme 1).<sup>[10]</sup>





Fig. 1. *cyclo*-Tri- and tetraphosphane  $(t-BuP)_n$  (n = 3 (4) or 4 (5)).

In this contribution we report on the transfer of a  $Ph_2P^+$ -moiety to **4** via the reaction with  $Ph_2PCl$  and  $GaCl_3$  or  $Me_3SiOTf$ .

The outcome of the reaction strongly depends on the employed halide abstracting reagent. In the same context, chloronium addition reactions to  $(t-BuP)_n$  (n = 3 (4), 4 (5), Fig. 1)

utilising the PCl<sub>5</sub>/GaCl<sub>3</sub> or PhICl<sub>2</sub>/Me<sub>3</sub>SiOTf system as Cl<sup>+</sup> source were investigated indicating, in part, complex reactions. Furthermore, in the course of our investigations we developed a protocol for the smooth conversion of the *cyclo*-polyphosphane (t-BuP)<sub>3</sub> (4) to (t-BuP)<sub>4</sub> (5) which is induced by Me<sub>3</sub>SiOTf.

## **Results and Discussion**

The slow addition of Ph2PCl to a C6H5F solution of 4 and GaCl3 yielded a yellow solution which was investigated by means of  ${}^{31}P{}^{1}H{}$  NMR spectroscopy (Fig. 2a). The spectrum shows only the resonances of an AM2X spin system with the relative intensities of 1:2:1 indicating the quantitative formation of the  $C_{\rm S}$ -symmetric *cyclo*-triphosphanylphosphonium ion 6<sup>+</sup>. The  ${}^{31}P{}^{1}H{}$  NMR spectroscopic parameters of  $6^+$  are summarised in Table 1. The addition of *n*-hexane to the reaction mixture leads to the precipitation of yellow, microcrystalline 6[GaCl<sub>4</sub>] which is conveniently isolated by filtration. Performing the same reaction, but using Me<sub>3</sub>SiOTf instead of GaCl<sub>3</sub> as the chloride abstracting agent, gives cation  $6^+$  only in a moderate yield of 35 % (Fig. 2b). The spectrum indicates complete consumption of 4 (absence of the AX<sub>2</sub> spin system;  $\delta(P_A) = -108.4$  ppm,  $\delta(P_X) = -70.0$  ppm,  ${}^{1}J_{AX} = -201.5 \text{ Hz})^{[11]}$  and two signals in addition to the resonances of the  $AM_2X$  spin system of cation  $6^+$  are observed. One of the prominent resonances is assigned to unreacted  $Ph_2PCl(\delta(P) =$ 82.0 ppm) and is not displayed in Fig. 1. The singlet resonance at high field ( $\delta(P) = -57.8 \text{ ppm}$ ) is assigned to tetrameric (*t*-BuP)<sub>4</sub> (5).<sup>[12]</sup> The AM<sub>2</sub>X spin system of cation  $6^+$  is consistent with a molecular arrangement in which the  $[Ph_2P]^+$ -moiety is located between both P atoms substituted with t-Bu-groups in a cisarrangement.<sup>[3b]</sup> The X part of the AM<sub>2</sub>X spin system is assigned to the tetra-coordinated P atom by comparison to related derivatives (Table 1; compare [Ph<sub>6</sub>P<sub>5</sub>][OTf]:  $\delta(P_X) = 22 \text{ ppm}$ ).<sup>[3c]</sup> The A and M<sub>2</sub> parts are assigned to the tri-coordinated P atoms.<sup>[3b-3d]</sup> Single crystals of 6[GaCl<sub>4</sub>] and 6[OTf] suitable for X-ray single

crystal structure determination were obtained by diffusion of *n*-hexane into concentrated  $C_6H_5F$  solutions of the salts at  $-30^{\circ}C$ . Table 2 shows crystallographic data and details of the structure refinement. The observed bond lengths and angles of the cations of both salts are almost equal, thus, only the structural parameters of cation  $6^+$  in  $6[GaCl_4]$  are discussed (Fig. 3).

The bond distances and angles are typical for *catena*phosphorus moieties and range from 2.1951(5) to 2.2352 (5) Å.<sup>[3,5]</sup> Cation **6**<sup>+</sup> shows a less puckered four-membered ring (average P–P–P–P torsion angle:  $\tau = 33.0(1)^{\circ}$ ) compared with **5** ( $\tau = 24.5(1)^{\circ}$ ).<sup>[13]</sup> Commonly, *cyclo*-tetraphosphanes exhibit an enhanced puckering in order to minimise steric interactions between substituents on non-adjacent phosphorus atoms. In contrast, *cyclo*-triphosphanylphosphonium ions are less puckered to minimise steric repulsion between the substituents at the tetra-coordinated P atom and both adjacent P atoms.<sup>[3b]</sup>

The formation of (t-BuP)<sub>4</sub> (5) in the reaction of 4, PhPCl<sub>2</sub>, and Me<sub>3</sub>SiOTf is unexpected. It is known that *cyclo*-polyphosphanes can undergo ring-inversion reactions in protic solvents to give thermodynamically more favoured ring-sizes.<sup>[14]</sup> However,

Table 1. <sup>31</sup>P{<sup>1</sup>H} NMR parameters of 6[GaCl<sub>4</sub>], 6[OTf], 8[GaCl<sub>4</sub>], and 8[OTf]

Spin system	<b>6</b> [GaCl <sub>4</sub> ] AM <sub>2</sub> X	<b>6</b> [OTf] AM <sub>2</sub> X	8[GaCl <sub>4</sub> ] AM <sub>2</sub> X	<b>8</b> [OTf] AM <sub>2</sub> X
$\delta(P_A)$	-22.2	-23.0	-40.9	-42.6
$\delta(P_M)$	-12.4	-13.0	-11.3	-11.1
$\delta(P_X)$	10.9	10.5	99.4	98.4
$^{1}J(P_{A}P_{M})$	-141.9	-141.7	-158.6	-158.0
$^{1}J(P_{M}P_{X})$	-277.3	-276.0	-330.7	-329.5
$^{2}J(\mathbf{P}_{A}\mathbf{P}_{X})$	-22.3	-22.4	8.2	7.0



**Fig. 2.**  ${}^{31}P{}^{1}H$  NMR spectra of the reaction mixtures of (*t*-BuP)<sub>3</sub> and Ph<sub>2</sub>PCl with (a) GaCl<sub>3</sub> or (b) Me<sub>3</sub>SiOTf in 1 : 1 : 1 stoichiometry (C<sub>6</sub>H<sub>5</sub>F, [D6]benzene capillary, 25°C); experimental (upwards) and fitted (downwards) AM<sub>2</sub>X spin system of **6**[GaCl<sub>4</sub>] and **6**[OTf]; the reaction equation in (b) is not balanced; unidentified side products are marked with asterisks.

	6[GaCl <sub>4</sub> ]	<b>6</b> [OTf]	9[GaCl <sub>4</sub> ]	8[GaCl <sub>4</sub> ]
Formula	C24H37Cl4GaP4	C <sub>25</sub> H <sub>37</sub> F <sub>3</sub> O <sub>3</sub> P <sub>4</sub> S	C16H37Cl4GaP4	C16H36Cl5GaP4
$M_{\rm r} [{\rm g}{\rm mol}^{-1}]$	660.94	598.49	564.86	599.30
Dimension [mm <sup>3</sup> ]	$0.12\times0.10\times0.08$	$0.15\times0.12\times0.05$	$0.16 \times 0.06 \times 0.04$	$0.09 \times 0.05 \times 0.04$
Colour, habit	Colourless, block	Colourless, block	Colourless, rod	Yellow, irregular
Crystal system	Triclinic	Monoclinic	Orthorhombic	Tetragonal
Space group	<i>P</i> -1	$P2_1/n$	Pnma	<i>I</i> -4
<i>a</i> [Å]	9.6669(7)	12.3446(5)	17.0102(7)	12.9276(2)
<i>b</i> [Å]	12.0355(9)	18.2397(8)	11.1070(5)	12.9276(2)
<i>c</i> [Å]	14.402(1)	13.7307(6)	14.7582(6)	8.2956(2)
α[°]	81.777(1)	90	90	90
β[°]	71.486(1)	104.233(1)	90	90
$\gamma$ [°]	86.940(1)	90	90	90
$V[Å^3]$	1572.5(2)	2996.7(2)	2788.3(2)	1386.38(5)
Z	2	4	4	2
<i>T</i> [K]	153(1)	153(2)	153(2)	153(2)
$\rho_c [\mathrm{gcm}^{-3}]$	1.396	1.327	1.346	1.436
F(000)	680	1256	1168	616
λ, Å	0.71073 (MoK <sub>α</sub> )	0.71073 (MoK <sub>α</sub> )	1.54178 (CuK <sub>α</sub> )	1.54178 (CuK <sub>α</sub> )
$\mu [{\rm mm}^{-1}]$	1.431	0.365	7.048	7.988
Absorption correction	SADABS	SADABS	SADABS	SADABS
Reflections collected	17567	30143	15358	3854
Reflections unique	8428	7130	2687	1231
R <sub>int</sub>	0.0201	0.0189	0.0619	0.0377
Reflection obs. $[F > 3\sigma(F)]$	7277	6366	2311	1209
Residual density [ $e Å^{-3}$ ]	0.651, -0.437	0.588, -0.432	0.704, -0.408	0.266, -0.279
Parameters	307	398	146	69
GOOF	1.042	1.037	1.070	1.055
$R_1 [I > 3\sigma(I)]$	0.0293	0.0336	0.0427	0.0288
$wR_2$ (all data)	0.0787	0.0937	0.1177	0.0727
CCDC number	931466	931567	931569	931568

Table 2. Summary of the crystallographic data of 6[GaCl<sub>4</sub>], 6[OTf], 9[GaCl<sub>4</sub>], and 8[GaCl<sub>4</sub>]



**Fig. 3.** Molecular structure of cation **6**<sup>+</sup> in **6**[GaCl<sub>4</sub>] (hydrogen atoms are omitted for clarity and thermal ellipsoids are displayed at 50 % probability). Selected bond lengths [Å] and angles [°]: P1–P2 2.1998(5), P2–P3 2.2350 (5), P3–P4 2.2352(5), P4–P1 2.1951(5), P1–C1 1.801(2), P1–C7 1.806(2), P2–C13 1.899(2), P3–C17 1.885(2), P4–C21 1.899(2); P1–P2–P3 83.17(2), P2–P3–P4 85.80(2), P3–P4–P1 83.27(2), P2–P1–C1 111.00(5), P2–P1–C7 119.13(5), P1–P2–C13 112.49(5), P2–P3–C17 104.08(6), P3–P4–C21 110.20(5), C1–P1–C7 108.43(7).

4 dissolved in  $C_6H_5F$  is stable for at least three weeks without any evidence of ring-interconversion to 5. Since this conversion process is not observed in the reaction involving GaCl<sub>3</sub>, we investigated the reaction of 4 and Me<sub>3</sub>SiOTf in  $C_6H_5F$  in a 1:1

ratio without the addition of  $Ph_2PCl$ . The reaction was monitored by  ${}^{31}P{}^{1}H{}$  NMR spectroscopy and the obtained spectra indicate that Me<sub>3</sub>SiOTf indeed promotes the reaction (Fig. 4).

The conversion is completed after 72 h. We speculate that the first step in the reaction is the formation of a complex between 4 and Me<sub>3</sub>Si<sup>+</sup>. The resulting cation may then dissociate to give *t*-Bu*P*=P*t*-Bu (which dimerises to **5**) and the phosphenium cation t-BuPSiMe<sub>3</sub><sup>+</sup> (which can insert into another molecule of 4), followed by release of Me<sub>3</sub>Si<sup>+</sup>. The conversion is significantly accelerated and completed within six hours if Me<sub>3</sub>SiOTf is present in  $\sim 10 \text{ mol-}\%$ . We suggest that in the 1:1 reaction  $(t-BuP)_3$  is completely consumed in adduct formation with Me<sub>3</sub>SiOTf. Thus, it is proposed that free (t-BuP)<sub>3</sub> is also involved in the conversion of 4 to 5. Variable temperature investigations are restricted due to the rather high melting point of  $C_6H_5F$  (Mp -42°C). Analytically pure 5 can be obtained quantitatively by removing all volatiles under vacuum from the reaction mixture. This method is interesting from a synthetic point of view since it allows for a convenient preparation of 5. Typically, a mixture of 4 and 5 is observed following standard synthetic routes which requires tedious and low-yielding separation procedures.[11]

The chloronium addition to **4** was investigated utilising  $[PCl_4][GaCl_4]$  as a chloronium ion source.<sup>[10]</sup> Thus, a suspension of  $[PCl_4][GaCl_4]$  in  $C_6H_5F$  was added to a solution of **4** in  $C_6H_5F$  according to Scheme 2.

The colour of the reaction mixture turned immediately orange and the formation of a large amount of orange precipitate of unknown constitution was observed. The supernatant solution was investigated by means of  ${}^{31}P{}^{1}H{}$  NMR spectroscopy.



Fig. 4.  ${}^{31}P{}^{1}H$  NMR spectra of the reaction of 4 and Me<sub>3</sub>SiOTf in a 1:1 stoichiometry over the course of 72 h (C<sub>6</sub>H<sub>5</sub>F, [D6]benzene capillary, 25°C).



**Scheme 2.** Reaction of **4** and  $[PCl_4][GaCl_4]$  (black): (a)  $+[PCl_4][GaCl_4]$ ,  $-PCl_3$ ,  $C_6H_5F$ , ambient temperature. A proposed reaction sequence for the formation of the observed product mixture (grey); the equation depicts the major products and is not balanced; anions of the products are not depicted as the products were only observed in solution.

The obtained spectrum indicates a complex product mixture by the observation of a large series of multiplet resonances of low intensities and three prominent singlet resonances. The singlet resonance at lowest field is assigned to  $PCl_3$  ( $\delta(P) = 220 \text{ ppm}$ ) indicating a successful Cl<sup>+</sup> transfer from PCl<sub>4</sub><sup>+</sup>. The remaining singlet resonances are assigned to *t*-BuPCl<sub>2</sub> ( $\delta(P) = 192 \text{ ppm}$ ) and the phosphonium ion t-Bu<sub>2</sub>PCl<sub>2</sub><sup>+</sup> ( $\delta(P) = 158 \text{ ppm}$ ).<sup>[15]</sup> The formation of t-BuPCl<sub>2</sub> can be rationalised by the intermediate formation of  $7^+$  formed via chloronium addition to 4 (Scheme 2). However,  $7^+$  decomposes via nucleophilic attack of Cl<sup>-</sup>. This leads to the formation of *t*-BuPCl<sub>2</sub> and formally disphosphene t-BuP=Pt-Bu which dimerises to tetraphosphane **5**. The formation of t-Bu<sub>2</sub>PCl<sub>2</sub><sup>+</sup> was previously observed in the reaction of t-Bu<sub>P</sub>Cl<sub>2</sub> and AlCl<sub>3</sub>.<sup>[15]</sup> Accordingly, it is assumed that t-Bu<sub>2</sub>PCl<sub>2</sub><sup>+</sup> forms via a GaCl<sub>3</sub>-mediated transfer of a t-Bugroup. The intermediary formed 2-methylpropan-2-ylium ion is assumed to act also as a proton source by expelling 2-methylprop-1-ene.<sup>[16]</sup> The proton is sequestered by the formed tetraphosphane 5 giving the corresponding cation  $9^+$ . This species was identified in the reaction mixture in small

amounts by its characteristic AM<sub>2</sub>X spin system in the proton decoupled <sup>31</sup>P NMR spectrum.<sup>[3d]</sup> In addition, cation  $9^+$ crystallised as the GaCl<sub>4</sub><sup>-</sup>-salt by layering the reaction mixture with *n*-hexane (-32°C) after four days. Cation  $9^+$  shows similar bond lengths and angles as observed for the corresponding triflate salt  $9[OTf]^{[3d]}$  and Table 2 shows crystallographic data and details of the structure refinement. The in situ formed tetraphosphane 5 reacts with PCl<sub>4</sub><sup>+</sup> via a chloronium transfer to cation  $8^+$  and PCl<sub>3</sub>. A small amount of  $8^+$  was confirmed in the reaction mixture by the observation of its characteristic AM<sub>2</sub>X spin system (Table 1). Analytically pure  $8[GaCl_4]$  can be obtained via the direct chloronium addition to 5 (see below).

Mixtures of PhICl<sub>2</sub> and Me<sub>3</sub>SiOTf were previously employed as versatile reagents for chloronium addition reactions.<sup>[10]</sup> Thus, **4** was also reacted with PhICl<sub>2</sub> and Me<sub>3</sub>SiOTf in a 1:1:1 stoichiometry in C<sub>6</sub>H<sub>5</sub>F (Fig. 5). The <sup>31</sup>P{<sup>1</sup>H} NMR spectrum of the reaction mixture shows resonances associated with the formation of mainly **5** together with *t*-BuPCl<sub>2</sub>.

Tetraphosphane **5** forms according to the Me<sub>3</sub>SiOTf-induced ring conversion reaction (see above). *t*-BuPCl<sub>2</sub> is obtained by



**Fig. 5.**  ${}^{31}P{}^{1}H$  NMR spectra of the reaction mixtures of (*t*-BuP)<sub>3</sub>, PhICl<sub>2</sub>, and Me<sub>3</sub>SiOTf in 1 : 1 : 1 stoichiometry (C<sub>6</sub>H<sub>5</sub>F, [D6]benzene capillary, 25°C); the equation is not balanced and anions of the products are not depicted as the products were only observed in solution.



**Fig. 6.**  ${}^{31}P{}^{1}H{}$  NMR spectra of the reaction mixtures of (a) (*t*-BuP)<sub>4</sub>, PCl<sub>5</sub>, and GaCl<sub>3</sub> and (b) (*t*-BuP)<sub>4</sub>, PhICl<sub>2</sub>, and Me<sub>3</sub>SiOTf, both in 1:1:1 stoichiometries (C<sub>6</sub>H<sub>5</sub>F, [D6]benzene capillary, 25°C); experimental (upwards) and fitted (downwards) AM<sub>2</sub>X spin system of **8**[GaCl<sub>4</sub>] and **8**[OTf].

the intermediary formation of  $7^+$  followed by subsequent degradation via nucleophilic attack of Cl<sup>-</sup> as depicted in Scheme 2. Furthermore, small amounts of cation  $9^+$  and *cyclo*-chlorotetraphosphane 10 were identified in the reaction mixture. Compound 10 was previously synthesised by the

insertion of in situ generated chlorophosphanediyl [P–Cl] in a P–P bond of 4.<sup>[17]</sup> A similar reaction might be proposed in this case. A chloro-group of *t*-BuPCl<sub>2</sub> is sequestered by Me<sub>3</sub>SiOTf accompanied by the elimination of a 2-methylpropan-2-ylium ion. This formally provides the [P–Cl] fragment which reacts

with 4 to give 10. As previously observed, the 2-methylpropan-2-ylium ion serves as a proton source and, therefore, the protonated tetraphosphane  $9^+$  is observed in the reaction mixture as well. The resonances of cation  $9^+$  in the  ${}^{31}P{}^{1}H{}$ NMR spectrum are not well resolved due to dynamic effects caused by additional Me<sub>3</sub>SiOTf in the reaction mixture. However, cation  $9^+$  was crystallised as the OTf<sup>-</sup>-salt by layering the reaction mixture with *n*-hexane ( $-32^{\circ}C$ ) for two days. The results of the X-ray investigation were identical to the already reported structure of 9[OTf].<sup>[3b]</sup>

The attempted chloronium addition to cyclo-triphosphane 4 indicated that cyclo-tetraphosphane 5 might be a suitable substrate in such a reaction. Thus, the reactions of 5 with  $PCl_5/$ GaCl<sub>3</sub> and PhICl<sub>2</sub>/Me<sub>3</sub>SiOTf in  $C_6H_5F$  were investigated. The <sup>31</sup>P <sup>1</sup>H} NMR spectra of the reaction mixtures are depicted in Fig. 6. In both cases the formation of cation  $8^+$  is indicated by its AM<sub>2</sub>X spin system (Table 1). The tetra-coordinated phosphorus atom resonates at lower field ( $\delta(P_A) = 99.4 \text{ ppm}$ ) compared with organo-substituted triphosphanylphosphonium ions.<sup>[3]</sup> This is caused by the -I effect of the chloro-substituent. In the case of GaCl<sub>3</sub> as the chloride abstracting agent the formation of  $8^+$  is almost quantitative and the corresponding GaCl<sub>4</sub>-salt was obtained in a high yield (85%) by addition of *n*-hexane to the reaction mixture and isolation of the formed precipitate. Single crystals of 8[GaCl<sub>4</sub>] were obtained by slow diffusion of *n*-hexane  $(-32^{\circ}C)$  into a C<sub>6</sub>H<sub>5</sub>F solution and details of the structure refinement and crystallographic data are shown in Table 2. The chlorine atom of the cation in 8[GaCl<sub>4</sub>] exhibits a four-fold positional disorder with a site occupancy factor of the chlorine atom of 0.25. Thus, structural parameters of the compound are not discussed; however, the constitution of the compound is verified. If PhICl<sub>2</sub> is used in combination with Me<sub>3</sub>SiOTf as a chloride abstracting agent only little conversion of 5 to  $8^+$  is observed (<25%). Next to unreacted starting material 5 the phosphane t-BuPCl<sub>2</sub> constitutes one of the main products (Fig. 6b). This is the result of nucleophilic degradation by chloride anions and renders Me<sub>3</sub>SiOTf as the less suitable chloride abstracting agent.

#### Conclusions

The insertion of a Ph<sub>2</sub>P<sup>+</sup>-phosphenium ion, derived from Ph<sub>2</sub>PCl and GaCl<sub>3</sub> or Me<sub>3</sub>SiOTf, into a P–P bond of (t-BuP)<sub>3</sub>, as well as halonium addition with chloronium ion sources PCl<sub>5</sub>/GaCl<sub>3</sub> or PhICl<sub>2</sub>/Me<sub>3</sub>SiOTf to (t-BuP)<sub>3</sub> and (t-BuP)<sub>4</sub>, was investigated. Both reactions reveal a strong dependency on the chloride abstracting reagent. GaCl<sub>3</sub> is the stronger halide abstracting reagent yielding quantitatively the cations [Ph<sub>2</sub>P(t-BuP)<sub>3</sub>]<sup>+</sup> (**6**<sup>+</sup>) and [(t-BuP)<sub>4</sub>Cl]<sup>+</sup> (**8**<sup>+</sup>) as gallate salts. Only moderate conversion is observed if Me<sub>3</sub>SiOTf is used. However, an interesting Me<sub>3</sub>SiOTf-mediated ring expansion reaction is unveiled allowing for the smooth conversion of (t-BuP)<sub>3</sub> to (t-BuP)<sub>4</sub>. This is important from a synthetic point of view since the elaborate separation of (t-BuP)<sub>n</sub> (n = 3, 4) can be avoided.

# Experimental

### General

All reactions were performed in a glove box produced by MBraun, or using Schlenk techniques under an inert atmosphere of purified Argon (purchased from Westfalen AG). Dry oxygen-free  $C_6H_5F$ ,  $CH_2Cl_2$  (drying agent: CaH<sub>2</sub>) and *n*-hexane (drying agent: sodium) were employed. Anhydrous deuterated dichlor-omethane ([D2]dichloromethane) was purchased from Sigma-Aldrich. All distilled and deuterated solvents were stored either

over 4 Å molecular sieves ([D2]dichloromethane,  $C_6H_5F$ ) or potassium mirror (n-hexane). Reagents such as PCl<sub>5</sub>, GaCl<sub>3</sub>, Me<sub>3</sub>SiOTf, and Ph<sub>2</sub>PCl were purchased from Sigma-Aldrich. Ph2PCl and Me3SiOTf were distilled before use. GaCl3 and PCl5 were sublimed before use. Reagents such as  $(t-BuP)_3$ ,<sup>[11]</sup>  $(t-BuP)_4$ ,<sup>[11]</sup> [PCl<sub>4</sub>][GaCl<sub>4</sub>],<sup>[10]</sup> and PhICl<sub>2</sub><sup>[18]</sup> were prepared according to known literature procedures. NMR spectra were measured on either a Bruker AVANCE III spectrometer (<sup>1</sup>H (400.03 MHz), <sup>13</sup>C (100.59 MHz), 71Ga (122.02 MHz), 19F (188.31 MHz) and <sup>31</sup>P (161.94 MHz)) or a Bruker AVANCE II spectrometer (<sup>1</sup>H (200.13 MHz), <sup>31</sup>P (81.01 MHz)) at 300 K unless otherwise specified. All <sup>13</sup>C NMR spectra were exclusively recorded with composite pulse decoupling. Chemical shifts were referenced to TMS  $\delta = 0.00 ({}^{1}\text{H}, {}^{13}\text{C}) \text{ or } H_{3}\text{PO}_{4} (85\%) \delta = 0.00$  $(^{31}P, \text{ externally})$ . Chemical shifts ( $\delta$ ) are reported in ppm. Coupling constants (J) are reported in Hz. Yields of products in solution were determined by integration of all resonances observed in the corresponding <sup>31</sup>P NMR spectra. For compounds which give rise to a higher order spin system in the  ${}^{31}$  D (11) N C  ${}^{1}P{}^{1}H$  NMR spectrum, the resolution enhanced  ${}^{31}P{}^{1}H$  NMR spectrum was transferred to the software gNMR, version 5.0, by Cherwell Scientific.<sup>[19]</sup> The full line shape iteration procedure of gNMR was applied to obtain the best match of the fitted to the experimental spectrum.  ${}^{1}J({}^{31}P{}^{31}P)$  coupling constants were set to negative values<sup>[20]</sup> and all other signs of the coupling constants were obtained accordingly. The designation of the spin systems were performed by convention. The spin system is considered to be higher order and consecutive alphabet letters are assigned if  $\Delta\delta(P_iP_{ii})^n J(P_iP_{ii}) < 10$ . For  $\Delta\delta(P_iP_{ii})^n J(P_iP_{ii})$ >10, the spin system is considered to be pseudo first order and the assigned letters are separated (alphabet). Melting points were recorded on an electrochemical melting point apparatus (Barnstead Electrothermal IA9100) in sealed capillaries under argon atmosphere and are uncorrected. Infrared (IR) and Raman spectra were recorded at ambient temperature using a Bruker Vertex 70 instrument equipped with a RAM II module (Nd: YAG laser, 1064 nm). The Raman intensities are reported in percent relative to the most intense peak and are given in parentheses. An attenuated total reflectance (ATR) unit (diamond) was used for recording IR spectra. The intensities are reported relative to the most intense peak and are given in parentheses using the following abbreviations: vw = very weak, w = weak, m = medium, s = strong, v = very strong. Elemental analyses were performed on a Vario EL III CHNS elemental analyser at the IAAC, University of Münster, Germany.

## $\boldsymbol{6}[GaCl_4]$

A solution of Ph<sub>2</sub>PCl (661.9 mg, 3.0 mmol) and GaCl<sub>3</sub> (528.2 mg, 3.0 mmol) in  $C_6H_5F$  (10 mL) was slowly added to a solution of (*t*-BuP)<sub>3</sub> (792.8 mg, 3.0 mmol) in C<sub>6</sub>H<sub>5</sub>F (10 mL). The yellow reaction mixture was stirred for 30 min at ambient temperature.  ${}^{31}P{}^{1}H{}$  NMR investigation of the reaction mixture indicated complete conversion to 6[GaCl<sub>4</sub>]. Upon addition of n-hexane (5 mL) the separation of orange oil was observed which solidified after removing the supernatant and adding n-hexane (5 mL) again. The orange solid was washed with *n*-hexane  $(3 \times 5 \text{ mL})$  and dried under vacuum yielding analytically pure, moisture and air-sensitive 6[GaCl<sub>4</sub>] (1.3 g, 66 %). Mp 160-163°C (Found: C 43.3, H 5.3. C<sub>24</sub>H<sub>37</sub>Cl<sub>4</sub>GaP<sub>4</sub> requires C 43.6, H 5.7 %); Raman v  $(200 \text{ mW})/\text{cm}^{-1}$  3060 (57), 2958 (33), 2896 (69), 1583 (75), 1459 (21), 1440 (12), 1168 (33), 1089 (28), 1027 (32), 999 (100), 617 (15), 575 (35), 550 (18), 498 (22), 345 (82), 227 (19), 187 (38), 162 (21), 150 (27);  $v_{max}$ (neat)/cm<sup>-1</sup> 3058 (vw), 2951 (s), 2858 (vw), 1734 (vw), 1716 (vw), 1698 (vw), 1684 (vw), 1653 (vw), 1558 (vw), 1541 (w), 1507 (vw), 1457 (m), 1438 (s), 1393 (w), 1364 (m), 1310 (w), 1156 (v.), 1097 (vw), 997 (m), 937 (w), 801 (m), 739 (s), 686 (m), 619 (vw), 593 (w), 548 (m), 502 (w), 471 (s); <sup>1</sup>H NMR ([D2]dichloromethane, 400.03 MHz)  $\delta$  1.30 (9H, d, P<sub>M</sub>C(CH<sub>3</sub>)<sub>3</sub>,  $^{3}J(\text{HP}_{\text{M}}) = 8.4 \text{ Hz}, 1.32 (9\text{H}, d, P_{\text{M}}C(CH_{3})_{3},$  $^{3}J(\mathrm{HP}_{\mathrm{M}}) =$ 8.4 Hz), 1.38 (9H, d,  $P_AC(CH_3)_3$ ,  ${}^3J(HP_A) = 14.3$  Hz), 7.66–7.96 (10H, m,  $P_X(C_6H_6)_2$ ); <sup>13</sup>C{<sup>1</sup>H} NMR ([D2]dichloromethane, 100.59 MHz)  $\delta$  29.4 (3C, dt, P<sub>X</sub>C(CH<sub>3</sub>)<sub>3</sub>, <sup>2</sup>J(CP<sub>X</sub>) = 15.9 Hz,  ${}^{3}J(CP_{M}) = 5.0 \text{ Hz}$ , 31.3 (6C, m,  $P_{M}C(CH_{3})_{3}$ ), 31.9 (1C, m,  $P_{X}C$ (CH<sub>3</sub>)<sub>3</sub>), 37.6 (2C, m, P<sub>M</sub>C(CH<sub>3</sub>)<sub>3</sub>), 117.6 (1C, m, *i*-Ph), 124.3  $(1C, m, i-Ph), 131.1 (2C, d, m-Ph, {}^{3}J(CP_{X}) = 2.2 Hz), 131.2 (2C, d)$ d, *m*-Ph,  ${}^{3}J(CP_{X}) = 2.3 \text{ Hz}$ , 133.5 (2C, dt, *o*-Ph,  ${}^{2}J(CP_{X}) =$ 9.9 Hz,  ${}^{3}J(CP_{M}) = 4.8$  Hz), 135.0 (1C, d, *p*-Ph,  ${}^{4}J(CP_{X}) = 3.5$  Hz), 135.6 (2C, dt, *o*-Ph,  ${}^{2}J(CP_{X}) = 10.1$  Hz,  ${}^{3}J(CP_{M}) = 4.7$  Hz), 136.1 (1C, d, *p*-Ph,  ${}^{4}J(CP_{X}) = 4.2 \text{ Hz}$ );  ${}^{71}\text{Ga}\{{}^{1}\text{H}\}$  NMR ([D2] dichloromethane, 122.02 MHz)  $\delta$  250.3 (s,  $\Delta v_{1/2} = 55$  Hz);  $^{31}P{^{1}H}$  NMR ([D2]dichloromethane, 161.94 MHz) AM<sub>2</sub>X spin system  $\delta(P_A) = -22.2$ ,  $\delta(P_M) = -12.4$ ,  $\delta(P_X) = 10.9$ ,  $J(P_A P_M) = -142 \text{ Hz}, \quad {}^{1}J(P_M P_X) = -277 \text{ Hz},$  $^{2}J(P_{A}P_{X}) =$ -22.3 Hz. Crystals of 6[GaCl<sub>4</sub>], which were suitable for single crystal X-ray structure determination, were obtained by diffusion of *n*-hexane into a  $C_6H_5F$  solution at  $-30^{\circ}C$ .

## **6**[OTf]

A solution of Ph<sub>2</sub>PCl (220.6 mg, 1.0 mmol) and Me<sub>3</sub>SiOTf (222.3 mg, 1.0 mmol) in  $C_6H_5F$  (3 mL) was slowly added to a solution of (t-BuP)<sub>3</sub> (264.3 mg, 1.0 mmol) in C<sub>6</sub>H<sub>5</sub>F (5 mL). The yellow reaction mixture was stirred for one hour at ambient temperature and investigated by means of  ${}^{31}P{}^{1}H$  NMR spectroscopy. The addition of n-hexane (5 mL) to the reaction mixture initiated the formation of a yellow microcrystalline material. The solid was washed with *n*-hexane  $(3 \times 3 \text{ mL})$  and dried under vacuum to yield analytically pure, moisture and airsensitive 6[OTf] (197 mg, 0.3 mmol, 33 %). Mp: 144-147°C (Found: C 49.7, H 5.6.  $C_{25}H_{37}F_3O_3P_4S$  requires C 50.2, H 6.2%); Raman v (200 mW)/cm<sup>-1</sup> 3061 (29), 2896 (36), 2185 (14), 2061 (17), 1584 (35), 1168 (17), 1089 (18), 1027 (18), 999 (33), 345 (100), 227 (33), 187 (19);  $v_{max}(neat)/cm^{-1}$  2950 (s), 1979 (vw), 1570 (vw), 1457 (m), 1438 (s), 1392 (w), 1364 (s), 1311 (w), 1165 (v.), 1098 (s), 997 (m), 936 (vw), 801 (m), 749 (vw), 738 (m), 687 (s), 619 (w), 593 (w), 548 (s), 501 (w), 471 (m); <sup>1</sup>H NMR ([D2]dichloromethane, 400.03 MHz) δ 1.30 (9H, d,  $P_MC(CH_3)_3$ ,  ${}^{3}J(HP_M) = 8.4 \text{ Hz}$ ), 1.32 (9H, d,  $P_MC(CH_3)_3$ ,  ${}^{3}J(\text{HP}_{\text{M}}) = 8.4 \text{ Hz}, 1.38 \text{ (9H, d, } P_{\text{A}}C(CH_{3})_{3},$  $^{3}J(\mathrm{HP}_{\mathrm{A}}) =$ 14.3 Hz), 7.66–7.96 (10H, m,  $P_X(C_6H_6)_2$ ); <sup>13</sup>C{<sup>1</sup>H} NMR ([D2] dichloromethane, 100.59 MHz) & 29.3 (3C, dt, P<sub>A</sub>C(CH<sub>3</sub>)<sub>3</sub>,  $^{2}J(CP_{A}) = 15.5 \text{ Hz}, \,^{3}J(CP_{M}) = 4.8 \text{ Hz}) \,31.1 - 31.3 \,(6C, m, P_{M}C)$ (CH<sub>3</sub>)<sub>3</sub>), 31.5–32.2 (1C, m, P<sub>A</sub>C(CH<sub>3</sub>)<sub>3</sub>), 37.3–37.8 (2C, m, P<sub>M</sub>C (CH<sub>3</sub>)<sub>3</sub>), 117.6 (1C, m, *i*-Ph), 124.3 (1C, m, *i*-Ph), 131.1 (2C, d, *m*-Ph,  ${}^{3}J(CP_{X}) = 1.3 \text{ Hz}$ , 131.2 (2C, d, *m*-Ph,  ${}^{3}J(CP_{X}) = 1.5 \text{ Hz}$ ), 133.5 (2C, dt, *o*-Ph,  ${}^{2}J(CP_{X}) = 11.1 \text{ Hz}$ ,  ${}^{3}J(CP_{M}) =$ 7.1 Hz), 135.0 (1C, d, *p*-Ph,  ${}^{4}J(CP_{X}) = 3.5$  Hz), 135.6 (2C, dt, *o*-Ph,  ${}^{2}J(CP_{X}) = 10.0 \text{ Hz}, {}^{3}J(CP_{M}) = 4.7 \text{ Hz}), 136.1 (1C, d, p-Ph,$  ${}^{*}J(CP_X) = 4.0 \text{ Hz};$  <sup>19</sup>F NMR ([D2]dichloromethane, 188.31 MHz)  $\delta$  -78.8 (s, CF<sub>3</sub>); <sup>31</sup>P{<sup>1</sup>H} NMR ([D6]benzene, 161.94 MHz): AM<sub>2</sub>X spin system  $\delta(P_A) = -23.1$ ,  $\delta(P_M) =$  $-13.0, \quad \delta(P_X) = 10.5, \quad {}^{1}J(P_AP_M) = -141 \text{ Hz}, \quad {}^{1}J(P_MP_X) =$ -275 Hz,  ${}^{2}J(P_{A}P_{X}) = -22$  Hz. Crystals of 6[OTf], which were suitable for single crystal X-ray structure determination, were obtained by diffusion of *n*-hexane into a  $C_6H_5F$  solution at  $-30^{\circ}C$ .

### Ring Expansion of (t-BuP)<sub>3</sub> in the Presence of Me<sub>3</sub>SiOTf

A: Me<sub>3</sub>SiOTf (222.3 mg, 1.0 mmol) was added to a solution of  $(t\text{-BuP})_3$  (264.3 mg, 1.0 mmol) in C<sub>6</sub>H<sub>5</sub>F (2 mL). The reaction mixture was stirred at ambient temperature and the reaction progress was monitored by  ${}^{31}P{}^{1}H{}$  NMR spectroscopy after 1, 12, 36, and 72 h.

**B:** Me<sub>3</sub>SiOTf (22.2 mg, 0.1 mmol) was added to a solution of (t-BuP)<sub>3</sub> (264.3 mg, 1.0 mmol) in C<sub>6</sub>H<sub>5</sub>F (2 mL). The reaction mixture was stirred at ambient temperature for 6 h. <sup>31</sup>P{<sup>1</sup>H} NMR investigation of the reaction mixture indicated complete conversion to (t-BuP)<sub>4</sub> (**5**).

In both cases 5 can be obtained quantitatively from the reaction mixtures by removing Me<sub>3</sub>SiOTf and  $C_6H_5F$  under vacuum.

## Reaction of (t-BuP)<sub>3</sub> with [PCl<sub>4</sub>][GaCl<sub>4</sub>]

A suspension of [PCl<sub>4</sub>][GaCl<sub>4</sub>] (384.3 mg, 1 mmol) in C<sub>6</sub>H<sub>5</sub>F (5 mL) was added in a single portion to a solution of (*t*-BuP)<sub>3</sub> (264.3 mg, 1.0 mmol) in C<sub>6</sub>H<sub>5</sub>F (5 mL). The reaction mixture turned immediately orange and an orange precipitate formed. The reaction mixture was stirred at ambient temperature for one hour. The supernatant solution was investigated by <sup>31</sup>P{<sup>1</sup>H} NMR spectroscopy. Crystals of **9**[GaCl<sub>4</sub>], which were suitable for single crystal X-ray structure determination, were obtained by diffusion of *n*-hexane into the filtered reaction mixture at  $-30^{\circ}$ C.

## Reaction of (t-BuP)<sub>3</sub> with PhICl<sub>2</sub> in the Presence of Me<sub>3</sub>SiOTf

A solution of PhICl<sub>2</sub> (274.9 mg, 1.0 mmol) in C<sub>6</sub>H<sub>5</sub>F (5 mL) was added dropwise to a solution of (t-BuP)<sub>3</sub> (264.3 mg, 1.0 mmol) and Me<sub>3</sub>SiOTf (222.3 mg, 1.0 mmol) in C<sub>6</sub>H<sub>5</sub>F (5 mL).The obtained yellow solution was stirred at ambient temperature for one hour. The reaction mixture was investigated by <sup>31</sup>P{<sup>1</sup>H} NMR spectroscopy.

# $\boldsymbol{8}[GaCl_4]$

A suspension of [PCl<sub>4</sub>][GaCl<sub>4</sub>] (1.54 g, 4.0 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (20 mL) was added to a solution of  $(t-BuP)_4$  (1.41 g, 4.0 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (15 mL) at -78°C within 30 min. The reaction mixture was warmed to ambient temperature, stirred for 30 min and investigated by means of <sup>31</sup>P{<sup>1</sup>H} NMR spectroscopy. Upon addition of *n*-hexane (40 mL) the precipitation of a pale yellow, microcrystalline solid was observed. The supernatant was removed and the solid was washed with *n*-hexane  $(2 \times 10 \text{ mL})$ and dried under vacuum yielding analytically pure, moisture and air-sensitive 8[GaCl<sub>4</sub>] (1.6 g, 2.7 mmol, 67%). Mp 160–161°C (Found: C 31.6, H 5.8. C16H36Cl5GaP4 requires C 32.1, H 6.1%); Raman v (200 mW)/cm<sup>-1</sup> 2963 (15), 2934 (11), 2897 (58), 1462 (21), 1441 (7), 1160 (15), 938 (8), 794 (19), 562 (26), 475 (7), 438 (19), 346 (38), 204 (9), 189 (20), 169 (7), 154 (100);  $v_{\text{max}}(\text{neat})/\text{cm}^{-1}2950(\text{s}), 2860(\text{vw}), 2341(\text{vw}), 2361(\text{m}), 1716$ (w), 1698 (vw), 1558 (vw), 1541 (w), 1507 (w), 1463 (s), 1394 (w), 1366 (m), 1245 (w), 1155 (v.), 1007 (m), 937 (w), 791 (m); <sup>1</sup>H NMR ([D2]dichloromethane, 400.03 MHz) δ 1.49 (9H, d,  $P_XC(CH_3)_3$ ,  ${}^3J(HP_X) = 24.0 Hz)$ , 1.51 (9H, d,  $P_AC(CH_3)_3$ ,  ${}^{3}J(\text{HP}_{\text{A}}) = 15.1 \text{ Hz}$ , 1.52 (18H, d,  $P_{\text{M}}C(CH_{3})_{3}$ ,  ${}^{3}J(\text{HP}_{\text{M}}) =$ 17.5 Hz); <sup>13</sup>C{<sup>1</sup>H} NMR ([D2]dichloromethane, 100.59 MHz) δ 23.2 (3C, td,  $P_XC(CH_3)_3$ ,  ${}^3J(CP_X) = 3.2$  Hz,  ${}^2J(CP_M) =$ 2.5 Hz), 28.8 (3C, dt,  $P_AC(CH_3)_3$ ,  ${}^2J(CP_A) = 15.7$  Hz,  ${}^{3}J(CP_{M}) = 5.0 \text{ Hz}), 30.0 (6C, ddd, P_{M}C(CH_{3})_{3}, {}^{2}J(CP_{M}) =$ 15.6 Hz,  ${}^{3}J(CP_{A}) = 6.4$  Hz,  ${}^{3}J(CP_{X}) = 4.4$  Hz), 32.4 (1C, ddt,  $P_AC(CH_3)_3$ ,  ${}^nJ(CP) = 29.5 \text{ Hz}$ ,  ${}^nJ(CP) = 17.7 \text{ Hz}$ ,  ${}^nJ(CP) = 13.4 \text{ Hz}$ , 40.1-40.7 (2C, m,  $P_MC(CH_3)_3$ ), 45.4-45.8 (1C, m,  $P_XC(CH_3)_3$ );  ${}^{71}Ga\{{}^{1}H\}\text{-NMR}$  ([D2]dichloromethane, 122.02 MHz)  $\delta$  250.1 (s,  $\Delta v_{1/2} = 52 \text{ Hz}$ ); <sup>31</sup>P{<sup>1</sup>H} NMR ([D2] dichloromethane, 166.94 MHz): AM<sub>2</sub>X spin system  $\delta(P_A) = -42.7$ ,  $\delta(P_M) = -11.1$ ,  $\delta(P_X) = 98.5$ , <sup>1</sup> $J(P_AP_M) = -157 \text{ Hz}$ , <sup>1</sup> $J(P_MP_X) = -330 \text{ Hz}$ , <sup>2</sup> $J(P_AP_X) = 8.8 \text{ Hz}$ . Crystals of **9**[GaCl<sub>4</sub>], which were suitable for single crystal X-ray structure determination, were obtained by diffusion of *n*-hexane into a CH<sub>2</sub>Cl<sub>2</sub> solution at  $-30^{\circ}$ C.

## Crystal Structures

Single crystals were coated with Paratone-N oil, mounted using a glass fibre pin and frozen in the cold nitrogen stream of the goniometer. X-ray diffraction data for compound 6[GaCl<sub>4</sub>]  $([Ph_2P(t-BuP)_3][GaCl_4])$  and 6[OTf]  $([Ph_2P(t-BuP)_3][OTf])$ were collected on a Bruker AXS APEX II CCD diffractometer equipped with a rotation anode at 153(2) K using graphitemonochromated MoK<sub> $\alpha$ </sub> radiation ( $\lambda = 0.71073$  Å) with a scan width of  $0.3^{\circ}$  and 15 s exposure time. The generator settings were 50 kV and 170 mA. X-ray diffraction data for compounds 8  $[GaCl_4]$  ([(t-BuP\_4)Cl][GaCl\_4]) and 9[GaCl\_4] ([(t-BuP\_4)H]) [GaCl<sub>4</sub>]) was collected on a Bruker SMART CCD diffractometer equipped with a rotation anode at 153(2) K using graphitemonochromated CuK<sub> $\alpha$ </sub> radiation ( $\lambda = 1.54178$  Å) with a scan width of 0.5° and 20/40 s exposure times. The generator settings were 45 kV and 110 mA. For all cases data reduction was done using the Bruker  $SMART^{[21]}$  software package. Data sets were corrected for absorption effects using SADABS routine (empirical multi-scan method). Structure solutions were found with the SHELXS-97 package using the direct method and were refined with SHELXL-97<sup>[22]</sup> against  $F^2$  using first isotropic and later anisotropic thermal parameters for all non-hydrogen atoms. Further details are summarised in Table 2 or can be obtained from the CCDC database with the respective CCDC reference number provided in Table 2. In the case of  $8[GaCl_4]$ ([t-Bu<sub>4</sub>P<sub>4</sub>Cl][GaCl<sub>4</sub>]) the chlorine atom of the cation exhibits a four-fold positional disorder. The s.o.f. (site occupancy factor) of the chlorine atom is 0.25. In 6[OTf] ([Ph<sub>2</sub>P(t-BuP)<sub>3</sub>][OTf]) the triflate anion is disordered over two positions with an s.o.f. of 52:48. Hydrogen atoms were generated with idealised geometries and isotropically refined using a riding model.

### Acknowledgements

We thank the Natural Sciences and Engineering Research Council of Canada, the Canada Research Chairs Program, the Canada Foundation for Innovation, the Walter C. Sumner Foundation, and the Nova Scotia Research and Innovation Trust Fund for funding. We also gratefully acknowledge the FCI (Liebig fellowship for M.H.H.), the European Phosphorus Science Network (PhoSciNet CM0802) and the DFG (WE 4621/2–1, travel stipend for D.K.).

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