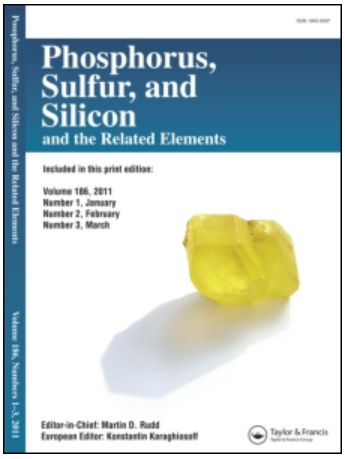

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New Look into the Synthesis of Polyhalogenoarylphosphanes

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New Look into the Synthesis of Polyhalogenoarylphosphanes

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*The present study shows new aspects of the synthesis of polyhalogenoarylphosphanes. The sterically hindered anions Ph(R)P-Y$^-$ (**1a–c**, Y = O, lone pair; R = Ph, Bu^t) have been used to show the complexity of the reaction between phosphorus nucleophiles and hexahalogenobenzenes or 9-bromofluorene (**E3**). The Ph(Bu^t)P-O$^-$ (**1a**) anion reacts with hexachlorobenzene (**E1**), hexafluorobenzene (**E2**), or **E3** to give Ph(R)P(O)X (**4a–c**, X = F, Cl, Br) with the release of the corresponding carbanion as a nucleofuge, followed by side reactions. In contrast, the lithium phosphides Ph(R)PLi (**1b**,**c**) react with hexahalogenobenzenes to give the corresponding diphosphanes **5a**,**b** as the main product and traces of* P*-arylated products, i.e., Ph(R)P-C_6X_5 (**10a**,**b**, X = Cl, F). Unexpectedly, Ph(Bu^t)PLi (**1b**) reacts with an excess of 9-bromofluorene to give only halogenophosphane Ph(Bu^t)P-X.*

Keywords Halogen–metal exchange; halogenobenzene; polyhalogenoarylphosphane; single-electron transfer (SET)

INTRODUCTION

The preparation of polyhalogenoarylphosphanes using phosphorus nucleophiles through various synthetic routes is well reported in the literature.[1,2] In these articles, the authors postulated that this transformation had the characteristics of a nucleophilic aromatic substitution. Neutral silyl and stannyl derivatives of three-coordinated phosphorus nucleophiles are convenient reagents, clearly giving the target products without side products.[1] On the other hand, negatively charged three-coordinate phosphorus nucleophiles possess a different reactivity.[2]

Bardin et al.[3] reported the reaction of *p*-R′C_6F_4Br with tris(diethylamino)phosphane in the presence of R_3MX (Scheme 1).

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This article is dedicated to Dr. Andrey Protchenko.
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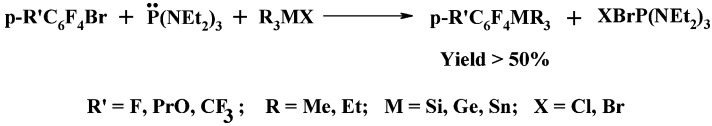


SCHEME 1

p-R′$C_6F_4MR_3$ was isolated with more than 50% yield, and the halogenated phosphorus nucleophile $(Et_2N)_3PXBr$ was obtained as the second product. It was observed that bromide or chloride was more easily taken off than fluoride. It was suggested that the rate-determining step was the cleavage of the Ar_F-X bond (X = halogen). Furthermore, no *P*-arylated product was identified. However, arylated silyl, germyl, and stannyl products were isolated, which could confirm the intermediate formation of an aryl anion, i.e., *p*-R′$C_6F_4^-$, in the reaction mixture.

Rachoń and colleagues[4a,b] postulated the possibility of the halogen transfer through a halophilic substitution in the reaction between the >P-O^- ambident phosphorus nucleophile and the C-Br bond of the benzyl bromide. The >P-O^- nucleophile attacks the C-Br bond of benzyl bromide by the soft phosphorus atom, giving >P(O)-Br. The first step of removing the halogen atom by the negatively charged phosphorus nucleophile could be a halogen–metal exchange type reaction, as first reported by Jones and Gilman.[5]

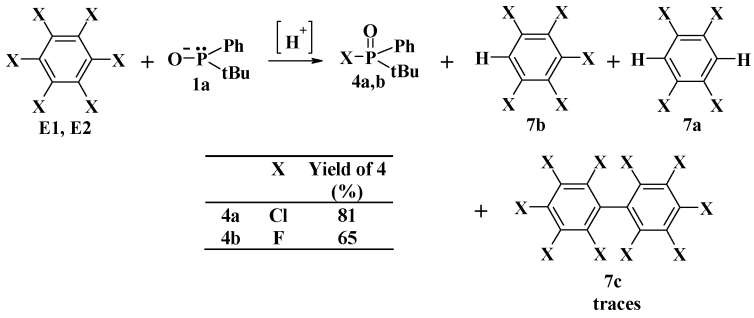
Bunnett[6] and Russell & Hershberger[7] showed that dialkyl phosphate anions participate in aromatic as well as in aliphatic $S_{RN}1$ processes. In contrast to the observations made by both authors, the current study demonstrates the formation of a phosphorus–halogen bond.

The reaction between negatively charged three-coordinated phosphorus nucleophiles and polychlorinated aromatic hydrocarbon compounds seems to occur in a different manner than a nucleophilic aromatic substitution. Experiments were performed in order to explore these unresolved issues.

RESULTS AND DISCUSSION

To look deeper into the reaction between phosphorus nucleophiles and hexahalogenobenzenes, negatively charged nucleophiles with steric hindrance at the phosphorus atom were chosen, i.e., Ph(R)P-Y^- (**1a–c**, Y = O, lone pair; R = Bu^t, Ph). Bulky carbon substituents should slow down side reactions for steric and electronic reasons. Moreover, such reagents should demonstrate higher nucleophilicity than neutral nucleophile or analogue compounds, which possess alkoxy or aryloxy

substituents at the phosphorus atom. Hexachlorobenzene (**E1**), hexafluorobenzene (**E2**), and 9-bromofluorene (**E3**) were chosen as electrophiles. Compound **E3** was chosen because it is much more susceptible to nucleophilic substitution than halogenoaryls. To compare the reactivity of various three-coordinate phosphorus nucleophiles towards hexahalogenated benzenes, a reaction between the potassium salt of *tert*-butylphenylphosphine oxide (**1a**) with **E1** was performed. The conversion was unambiguous and gave a halogenated phosphorus product, namely *tert*-butylphenylphosphinic acid chloride (**4a**) with 81% yield, as well as pentachlorobenzene (**7b**) with 41% yield, 1,2,4,5-tetrachlorobenzene (**7a**) with 6% yield, and traces of decachlorobiphenyl (**7c**) (Scheme 2). The final products suggest that the three-coordinate phosphorus atom attacked **E1** at the chlorine atom to give **4a** and $C_6Cl_5^-$ as a leaving group with a characteristic deep violet color. Subsequently the $C_6Cl_5^-$ anion participates in side reactions, probably via single electron transfer (SET), to give **7c** or **7a**. Similar results were obtained in the reaction between **1a** and **E2**. No *P*-arylated product was observed among the final products.



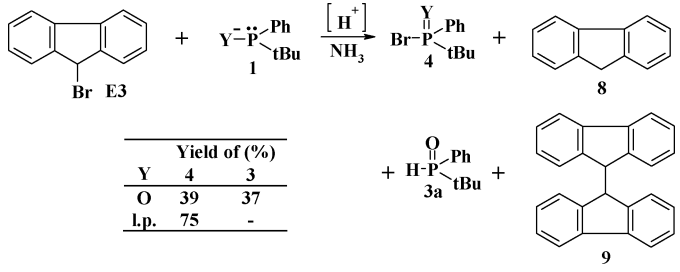
	X	Yield of 4 (%)
4a	Cl	81
4b	F	65

SCHEME 2

The reaction between C_6X_6 (X = halogen) and negatively charged three-coordinated phosphorus nucleophiles results in the formation of products with a phosphorus halogen bond, such as $Ph(Bu^t)P(O)$-X (**4a**,**b**, X = Cl, F).

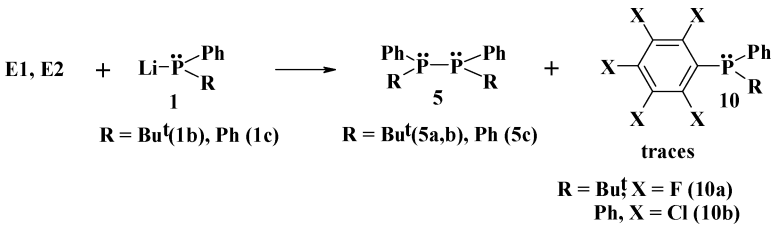
A comparison of nucleophilic substitution at the benzyl and aromatic carbon atoms was made by reacting **1a** with **E3**. The negatively charged three-coordinate phosphorus nucleophile **1a** should easily undergo a nucleophilic substitution with benzyl bromide. However in the case of the related 9-bromofluorene (**E3**), the phosphorus atom attacks the bromine atom of the C-Br bond to give *tert*-butylphenylphosphinic acid bromide (**4c**) and fluorenyl anion as a leaving group, which subsequently participates in a SET reaction to

form 9,9′-bifluorenyl (**9**). In fact the reaction produced **4c** with 39% yield and *tert*-butylphenylphosphine oxide (**3a**) with 37% yield, **9** with 82% yield, and fluorine (**8**) with 6% yield (Scheme 3). It is important to note that the phosphorus compounds were isolated in similar molar amounts. Dimerization products such as **9** or **7c** indirectly confirm the presence of an aryl anion in the reaction mixture and a single-electron transfer (SET) mechanism operating. The above observations further support the halophilic substitution mechanism reported by Rachoń and colleagues.[4a,b]



SCHEME 3

The lithium salts of *tert*-butylphenylphosphane (**1b**) and diphenylphosphane (**1c**) show a very different reactivity towards **E1** and **E2**. The corresponding diphosphanes [1,2-di-*tert*-butyl-1,2-diphenyldiphosphane (**5**) (mixture of *meso* and *rac* isomer in a 7:1 ratio) or 1,1,2,2-tetraphenyldiphosphane (**5c**)] and traces of *P*-arylated products [i.e., *tert*-butylphenyl(pentafluorophenyl)phosphane (**10a**) or diphenyl(pentachlorophenyl)phosphane (**10b**)] were identified among the final products (Scheme 4). These results demonstrate the different type of reactivity of the nucleophiles **1b** and **1c**. It is possible that both nucleophiles participate in the transfer of electrons to the hexahalogenobenzenes, as is postulated by Bunnett[6] and Russell & Hershberger.[7]



SCHEME 4

Compared to **1a** (shown in Scheme 2), **1b** possesses stronger nucleophilicity, which, however, did not go thorough a mechanism to generate *tert*-butylphenyl(9-fluorenyl)phosphane when reacted with excess of **E3** that was treated as an analogue of benzyl bromide. Similarly to **1a**, **1b** exclusively gave *tert*-butylbromophenylphosphane (**4d**) (Scheme 3), without any *P*-arylated product or diphosphane **5a**,**b** observed.

Compound **4d** was conveniently identified by $^{31}P\{^{1}H\}$ NMR spectroscopy. In analogy to the previous experiments, compounds with phosphorus halogen bonds, i.e., **4d** and **9** (Scheme 3), were observed. Using an excess of 9-bromofluorene (5 equiv.) allowed us to avoid side reactions between the nucleophile **1b** and the newly produced **4d**. The presence of the bromophosphane **4d** was fully confirmed by an independent reaction between **5a**,**b** and bromine.

CONCLUSION

The direct reactions between negatively charged three-coordinated phosphorus nucleophiles such as $Ph(Bu^t)P\text{-}O^-$ with hexahalogenobenzenes or 9-bromofluorene result in the formation of halogenated phosphorus products such as $Ph(Bu^t)P(O)X$ (**4**, X = F, Cl, Br) and corresponding carbanions, which subsequently participate in side reactions. The presented results suggest that instead of an S_NAr mechanism, the dehalogenation reaction occurs through a halophilic substitution (or halogen–metal exchange) by a single-electron transfer (SET) mechanism. No *P*-arylated products were observed in the reaction with the potassium salt of *tert*-butylphenylphosphine oxide (**1a**). Similarly, in the reaction with the excess of 9-bromofluorene (**1c**) exclusively gave **4d** without any *P*-arylated products. In contrast, **1b** and **1c** reacted with an excess of **E1** or **E2** gave the diphosphanes **5a**,**b** (as a mixture of *meso* and *rac* isomer), and **5c**, respectively, as well as traces of the *P*-arylated products **10a** or **10b**, which suggest in this case a $S_{RN}1$ processes.

EXPERIMENTAL

All experiments were carried out in an atmosphere of dry argon, using Schlenk techniques. Solvents were dried by usual methods (benzene and THF over benzophenone ketyl, $CHCl_3$ over P_2O_5, hexane over sodium–potassium alloy), distilled, and degassed. Chromatography was carried out on silica gel 60 (0.15–0.3 mm) Machery Nagel. For GC/MS, a Gas Chromatograph 5890 Seriess II with MSD 9772 SERIES (GC-MS) with autosampler (Hewlett-Packard) was used. NMR spectra

were obtained with a Varian Gemini 500 instrument operating at 500 MHz (^{1}H) and at 202.4 MHz (^{31}P). All J values are given in Hz. ^{31}P NMR spectra were obtained using broadband ^{1}H decoupling, and chemical shifts are reported relative to 85% H_3PO_4 as external standard. Mass spectra were obtained with a MASPEC II system [II32/99D9] in EI mode and, where necessary, the liquid SIMS technique was applied.

Reagents **1a–c** were generated according to procedures described in the literature.[9a,b]

Reaction of Potassium Salt of 1a with E1, E2, and E3

Potassium (0.39 g, 10 mmol) was dissolved in a mixture composed of liquid ammonia (25 mL) and THF (25 mL). The reaction mixture was stirred to complete dissolution of the metal. After cooling to –78°C, **4a** (1.08 g, 5 mmol) in THF (5 mL) was added, and the reaction mixture was stirred at –78°C for additional 30 min. Then **E1**, **E2**, or **E3** (5 mmol) in THF (40 mL) was added, and immediately a violet (in the case of **E3** a red) color appeared. After 3 h, NH_4Cl (1.5 g) was added, and the ammonia was evaporated at 10 mm Hg. The residue was poured into a mixture of toluene and aqueous $KHSO_4$ solution (25 mL). The water layer was extracted with toluene, and the combined organic phase was dried over $MgSO_4$. The solvent was evaporated, and the product was purified by crystallization and chromatography.

Products from the Reaction of 1a with E1

7a: 0.060 g (0.3 mmol, 6%), t_r = 6.75 min, GC/MS: (EI) M^+ 216; **7b:** 0.514 g (2.0 mmol, 41%), t_r = 7.90 min, GC/MS: (EI) M^+ 250; **7c:** (traces), t_r = 15.16 min, GC/MS: (EI) M^+ 430; **4a:** ($CHCl_3$) 0.877 g (4.0 mmol, 81%); ^{1}H NMR ($CDCl_3$): δ = 1.15 (d, $^3J_{PH}$ = 19 Hz, 9H, Bu^t), 7.10–7.77 (m, 5H, arom-H); ^{31}P{^{1}H} NMR (C_6D_6): δ = 72.2.[8,9]

Products from the Reaction of 1a with E2

***tert*-Butylphenylphosphinic acid fluoride** (**4b**)**:** 0.651 g (3.2 mmol, 65%); ^{1}H NMR ($CDCl_3$): δ = 1.23 (d, $^3J_{PH}$ = 17 Hz, 9H, Bu^t), 7.55–7.83 (m, 5H, arom-H); ^{31}P{^{1}H} NMR (C_6D_6): δ = 61.4 (d, $^1J_{PF}$ = 1052 Hz);[10] **1,2-di-*tert*-butyl-1,2-diphenyldiphosphane 1,2-dioxide** (**6a,b**): ($CHCl_3$:MeOH = 50:1); **6a**: 0.130 g (0.4 mmol, 14%); mp_{meso} = 205°C; ^{1}H NMR ($CDCl_3$): δ_{meso} = 0.98 (d, $^3J_{PH}$ = 16 Hz, 18H, Bu^t), 7.40–8.45 (m, 10H, arom-H); ^{31}P{^{1}H} NMR ($CDCl_3$): δ_{meso} = 39.8; MS: (SIMS) M^+ 362; **6b:** 0.061 g (0.1 mmol, 7%); mp_{rac} = 192–193°C; ^{1}H NMR ($CDCl_3$): δ_{rac} = 1.38 (d, $^3J_{PH}$ = 17 Hz, 18H, Bu^t), 7.00–7.80 (m, 10H, arom-H); ^{31}P{^{1}H} NMR ($CDCl_3$): δ_{rac} = 50.7; MS: (SIMS) M^+ 362;[8] ***tert*-butylphenylphosphinic acid** (**2**)**:** (traces), mp = 155–156°C; ^{1}H

NMR ($CDCl_3$): $\delta = 0.93$ (d, $^3J_{PH} = 15$ Hz, 9H, Bu^t), 6.93–7.57 (m, 5H, arom-H), 11.0 (s, 1H, OH); ^{31}P NMR ($CDCl_3$): $\delta = 52.0$.[8]

Products from the Reaction of 1a with E3

8: (hexane) 0.045 g (0.3 mmol, 6%); mp 116–118°C; ^1H NMR ($CDCl_3$): $\delta = 3.93$ (s, 2H, CH_2), 7.28–7.50 (m, 4H, arom-H), 7.56 (d, $J = 7.2$ Hz, 2H, arom-H), 7.82 (d, $J = 7.5$ Hz, 2H, arom-H); **9:** (hexane) 0.677 g (2.0 mmol, 82%); mp 248–249°C; ^1H NMR ($CDCl_3$): $\delta = 4.60$ (s, 2H, CH), 6.86 (d. $J = 7.0$ Hz, 4H, arom-H), 7.00 (t, $J = 7.4$ Hz, 4H, arom-H), 7.18 (t, $J = 7.5$ Hz, 4H, arom-H), 7.48 (d, $J = 7.7$ Hz, 4H, arom-H); **2c:** ($CHCl_3$:MeOH = 50:1), (Kugelrohr, 136°C/0.5 mm Hg), 0.509 g (1.9 mmol, 39%); ^1H NMR ($CDCl_3$): $\delta = 1.03$ (d, $^3J_{PH} = 16$ Hz, 9H, Bu^t), 7.10–7.77 (m, 5H, arom-H); $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta = 73.5$.[8] **3a:** ($CHCl_3$:MeOH = 50:1), 0.337 g (2.0 mmol, 37%), ^1H NMR ($CDCl_3$): $\delta = 1.13$ (d, $^3J_{PH} = 15$ Hz, 9H, Bu^t), 6.70 (d, $J_{PH} = 440$ Hz, 1H, PH), 6.83–7.67 (m, 5H, arom-H); ^{31}P NMR ($CDCl_3$): $\delta = 46.0$ (d, $J_{PH} = 440$ Hz).[9b]

Synthesis of *tert*-Butylbromophenylphosphine (4d)

To freshly prepared potassium naphthalenide (5 mmol) in 25 mL of THF at –78°C, *tert*-butylphenylchlorophosphane (**4f**) (1.003 g, 5 mmol) in THF (5 mL) was added. The reaction mixture was stirred until the disappearance of the green color. After 3 h at r.t., a sample of the reaction mixture was taken, C_6D_6 was added, and the $^{31}P\{^1H\}$ NMR spectrum was recorded. The $^{31}P\{^1H\}$ NMR spectrum of the reaction mixture showed two resonance lines attributable to 1,2-di-*tert*-butyl-1,2-diphenyldiphosphane (**5a**,**b**) ($\delta = 2.9$ and –3.5 ppm). The solution of **5a**,**b** was treated with bromine (0.80 g, 5 mmol), and after 3 h a sample of the reaction mixture was analyzed by ^{31}P NMR. The spectrum showed a resonance line attributable to **4d** ($\delta = 109.9$ ppm).

Reaction of 1b,c with E1, E2, or E3

tert-Butylphenylphosphane (**3b**) or diphenylphosphane (**3c**) (5 mmol) was dissolved in THF (20 mL). The solution was cooled to –78°C, and BuLi (2.2 mL, 2.5 M) in hexane was added. The reaction mixture was stirred at r.t. for 1 h, followed by the addition of **E1**, **E2**, or **E3** (25 mmol) in THF (45 mL). After 3 h, a sample of the reaction mixture was taken, C_6D_6 was added, and the $^{31}P\{^1H\}$ NMR spectrum was recorded (for the identified products see below). To fully confirm the identity of **4d** both samples, that from the reaction mixture and that from an independent

synthesis, were mixed together and the $^{31}P\{^{1}H\}$ NMR spectrum was recorded. It showed the presence of only one signal at $\delta = 109.9$ ppm. In the case of **E2** resonance lines attributable to **5a**,**b** ($\delta = 2.9$ and –3.5 ppm) and to **10a** ($\delta = 1.6$, m, P-C_6F_5) were observed. In the case of **E1**, the ^{31}P NMR spectrum showed resonance lines attributable to **5c** ($\delta = -15.1$ ppm) and to **10b** ($\delta = 10.7$, quintet, $^{3}J_{PH} = 7.3$ Hz, P-C_6H_5). Subsequently, dry air was passed through the reaction mixture in both experiments, which was then poured into a mixture of toluene and aqueous $KHSO_4$. The water layer was extracted with toluene (20 mL), and the combined organic phase was dried over $MgSO_4$. The solvent was evaporated, and the product was purified by crystallization and chromatography.

Products from the Reaction of 1b with E3

4c: 1.018 g (4.0 mmol, 78%); (Kugelrohr, 136°C/0.5 mm Hg); ^{1}H NMR ($CDCl_3$): $\delta = 1.03$ (d, $^{3}J_{PH} = 16$ Hz, 9H, Bu^t), 7.10–7.77 (m, 5H, arom-H), ^{31}P NMR ($CDCl_3$): $\delta = 73.5$.[8]

Products from the Reaction of 1b with E2

6a: 0.471 g (1.3 mmol, 51%); **6b:** 0.181 g (0.5 mmol, 19%).

Products from the Reaction of 1c with E1

Tetraphenyldiphosphane P,P′-dioxide (**6c**): 1.126 g (2.8 mmol, 56%), mp = 168–169°C; ^{1}H NMR ($CDCl_3$/DMSO): $\delta = 6.90$–6.99 (m, 6H, arom-H), 7.81–7.85 (m, 4H, arom-H), $^{31}P\{^{1}H\}$ NMR ($CDCl_3$/DMSO): $\delta = 24.9$.[8]

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