

## Video Article

# Preparation and Reactivity of a Triphosphenium Bromide Salt: A Convenient and Stable Source of Phosphorus(I)

Stephanie C. Kosnik<sup>1</sup>, Justin F. Binder<sup>1</sup>, Maxemilian C. Nascimento<sup>1</sup>, Charles L. B. Macdonald<sup>1</sup>
<sup>1</sup>Department of Chemistry and Biochemistry, University of Windsor

Correspondence to: Charles L. B. Macdonald at [cmacd@uwindsor.ca](mailto:cmacd@uwindsor.ca)

URL: <https://www.jove.com/video/55021>

DOI: [doi:10.3791/55021](https://doi.org/10.3791/55021)

Keywords: Chemistry, Issue 117, phosphorus, low valent, low oxidation state, main group, carbenes, inorganic, reagent, ligand

Date Published: 11/22/2016

Citation: Kosnik, S.C., Binder, J.F., Nascimento, M.C., Macdonald, C.L. Preparation and Reactivity of a Triphosphenium Bromide Salt: A Convenient and Stable Source of Phosphorus(I). *J. Vis. Exp.* (117), e55021, doi:10.3791/55021 (2016).

## Abstract

We present herein the optimized synthesis of a triphosphenium bromide salt. Apart from being a versatile metathesis reagent, this unusually stable low-valent-phosphorus-containing compound acts as a useful  $P^+$  transfer agent. Unlike traditional methods employed to access low-coordinate phosphorus species which usually require pyrophoric phosphorus-containing precursors (white phosphorus, Tris(trimethylsilyl)phosphine, etc.), or harsh reducing agents (alkali metals, potassium graphite, etc.), the current approach does not involve pyrophoric or explosive reagents and can be done on large scales (>20 g) in excellent yields by undergraduates with basic air-free synthetic training. The bromide counter ion is readily exchanged with other anions such as tetraphenyl borate (described herein) using typical salt metathesis reagents to obtain materials with desired properties and reactivities. The versatility of this  $P^+$  transfer approach is exemplified by the reactions of these triphosphenium precursors with an N-heterocyclic carbene and an anionic bisphosphine, each of which readily displace the neutral bisphosphine to give an NHC-stabilized phosphorus(I) cation and a phosphorus(I) containing zwitterion, respectively.

## Video Link

The video component of this article can be found at <https://www.jove.com/video/55021/>

## Introduction

The chemistry of main group elements in unusually low oxidation or valence states has been an area of significant interest over the last two decades.<sup>1</sup> Aside from the fundamental interest arising from their unique bonding and structure, such compounds often display reactivities that are very different from those of their more typical oxidation state counterparts. In this sense, they offer significant potential as reagents to build more complex main group-element containing materials.

A landmark class of low-valent phosphorus containing molecules are "triphosphenium" cations which were first reported by Schmidpeter in the 1980s.<sup>2</sup> These ions feature a dicoordinate phosphorus(I) ion ligated by two phosphonio substituents, with the more stable variants built from a chelating framework.<sup>3,4</sup> Our group has optimized the syntheses of triphosphenium halide salts<sup>5-7</sup> and has demonstrated that these stable compounds are versatile  $P^+$  transfer agents that are useful for the controlled synthesis of phosphorus(I)-containing oligomers,<sup>8</sup> zwitterions,<sup>9</sup> and phosphamethine cyanine dyes.<sup>10,11</sup> While the original syntheses of such compounds often involve dangerous phosphorus-containing reagents and/or highly reducing conditions, the controlled route we present is safe, P-atom efficient, and convenient. The method results in high purity materials which may be used as dyes, ligands for transition metal complexes and precursors for more complex phosphorus-containing species.

## Protocol

NOTE: Deuterated solvents were dried according to literature procedure when necessary, and all other solvents were dried over a series of Grubbs'-type columns<sup>12</sup> and degassed prior to use. Potassium 1,2,4-tris(diphenylphosphino)cyclopentadiene  $[K][(\text{Ph}_2\text{P})_3\text{C}_5\text{H}_2]$  and the N-heterocyclic carbene 1,3,4,5-tetramethylimidazole-2-ylidene ( $^{\text{Me}}\text{NHC}^{\text{Me}}$ ) were synthesized according to literature procedures and the latter was sublimed prior to use.<sup>9,13</sup> Cyclohexene was dried over  $\text{CaH}_2$ , distilled and degassed prior to use. Acetonitrile- $\text{d}_3$  ( $\text{CD}_3\text{CN}$ ) and dichloromethane- $\text{d}_2$  ( $\text{CD}_2\text{Cl}_2$ ) were dried over phosphorus pentoxide and degassed prior to use. Diatomaceous earth was dried in an oven at 150 °C overnight prior to use. All other reagents were used as received.

## 1. Synthesis of $[\text{dppeP}][\text{Br}]$

1. Dissolve 1.00 g of 1,2-bis(diphenylphosphino)ethane (dppe) in approximately 40 ml of anhydrous, degassed dichloromethane (DCM) in a 250 ml Schlenk flask, under inert gas, equipped with a rubber septum.
2. By syringe or cannula transfer, add 2.53 ml of dry, degassed, cyclohexene to the Schlenk flask containing the stirring solution of dppe.
3. To this solution, add 0.26 ml of  $\text{PBr}_3$  via syringe, dropwise with vigorous stirring. The solution should immediately turn pale yellow, and white precipitate forms after stirring the solution for 20 min. Allow the reaction to stir for several hours or overnight.

- After stirring for several hours or overnight, filter the reaction mixture through a fritted flask topped with a one-inch thick diatomaceous earth plug to remove the precipitate.
- Collect the resulting solution and remove the DCM under vacuum on a Schlenk line.
- To the resulting oil, add approximately 75 ml of tetrahydrofuran (THF) while stirring vigorously (or sonicating) to precipitate the product as a white solid.
- Immediately after the white precipitate forms, collect it via filtration with a fritted flask under an inert atmosphere. Collect the solid immediately, and do not leave the suspension to stir for more than 30 min.
- Once collected, dissolve a small amount of [dppeP][Br] in  $\text{CD}_2\text{Cl}_2$  or  $\text{CDCl}_3$  to obtain  $^{31}\text{P}$ ,  $^1\text{H}$  and  $^{13}\text{C}$  NMR to confirm purity. [dppeP][Br] can be stored indefinitely in an inert atmosphere, or for several weeks on the benchtop.<sup>6</sup>

## 2. Synthesis of [dppeP][BPh<sub>4</sub>]

- Dissolve 0.5 g of [dppeP][Br] salt in 5 ml of DCM, in a Schlenk flask. Stir the solution under nitrogen gas. Then, add 0.35 g of sodium tetraphenylborate in 5 ml of THF.
- Allow the solution to stir for several hours or overnight, until a fine precipitate forms.
- Centrifuge the suspension to eliminate the precipitate (KBr) and remove the solvent under reduced pressure to yield [dppeP][BPh<sub>4</sub>] as a white powder.

## 3. Synthesis of [<sup>Me</sup>NHC<sup>Me</sup><sub>2</sub>P][BPh<sub>4</sub>]

- Load a 100 ml Schlenk flask with 0.200 g of <sup>Me</sup>NHC<sup>Me</sup> and a stir bar under an inert atmosphere.
- Load a 100 ml round bottom flask with 0.603 g of [dppeP][BPh<sub>4</sub>] under an inert atmosphere.
- Cannula transfer 20 ml of THF to the Schlenk flask containing 0.200 g of <sup>Me</sup>NHC<sup>Me</sup> and begin magnetic stirring.
- Cannula transfer 20 ml of THF to the 100 ml round bottom flask with 0.603 g of [dppeP][BPh<sub>4</sub>] and stir until dissolved.
- Cannula transfer the solution of [dppeP][BPh<sub>4</sub>] in THF to the stirring solution of <sup>Me</sup>NHC<sup>Me</sup> in THF and allow the yellow solution to stir for 1 hr.
- Concentrate the yellow solution to a third of the original volume (13 ml) under reduced pressure.
- Add diethyl ether (Et<sub>2</sub>O) (40 ml) to the stirring concentrated solution to initiate precipitation of the yellow product and allow the resultant suspension to stir for 20 min.
- Place a sealed frit fitted attached to a 100 ml Schlenk flask on the Schlenk line and create an inert atmosphere by evacuating the flask using vacuum and refilling the flask with nitrogen from the Schlenk line. Evacuate for 5 min and refill with nitrogen 3 times to insure an inert atmosphere.
- Cannula transfer the Et<sub>2</sub>O suspension into the apparatus and filter the precipitate.
- Wash the precipitate with 10 ml of Et<sub>2</sub>O three times and allow the precipitate to dry under reduced pressure for 2 hr.
- Optional) Allow the filtrate and washings to evaporate slowly under nitrogen to recrystallize dppe. Wash the crystals with a minimal amount of hexanes, dry, and collect the crystals for re-use.

## 4. Synthesis of (Ph<sub>2</sub>P)C<sub>5</sub>H<sub>2</sub>(Ph<sub>2</sub>P)<sub>2</sub>P

- To a 150 ml Schlenk flask containing 0.484g [dppeP][Br] in an inert atmosphere, add 40 ml of dry, degassed THF.
- Place the Schlenk in a dry-ice/acetone bath to cool the suspension to -78 °C.
- Cannula transfer a THF solution of 0.625g [K][(Ph<sub>2</sub>P)<sub>3</sub>C<sub>5</sub>H<sub>2</sub>] in a round bottom flask, to the Schlenk flask containing [dppeP][Br].
- When the addition is complete, remove the Schlenk flask from the acetone bath and allow to warm to room temperature. After stirring for 2 hr, the solution will be light yellow with a white precipitate present.
- Transfer the suspension to an air-free fritted filter equipped with a 150 ml Schlenk flask, to remove the white precipitate (KBr).
- Collect the yellow solution and remove the THF under vacuum.
- Add an 80:20 mixture of dry and degassed diethyl ether:pentane to the resulting oil and allow to stir for 20 min.
- Collect the product (Ph<sub>2</sub>P)C<sub>5</sub>H<sub>2</sub>(Ph<sub>2</sub>P)<sub>2</sub>P as a pale yellow precipitate by filtering the suspension through an air-free, fritted flask. The remaining ether/pentane solution contains the dppe impurity and may be discarded or the solvent may be removed under vacuum and the dppe collected for further use.

## Representative Results

A stable salt ([dppeP][Br]) containing a low valent phosphorus(I) source can be synthesized easily by the addition of  $\text{PBr}_3$  to diphenylphosphinoethane (dppe) in the presence of excess cyclohexene (Figure 1)<sup>6</sup>.

Upon work up of the reaction,  $^{31}\text{P}$  NMR spectra show the presence of a triplet signal that is significantly shielded at -220 ppm, and a doublet signal at 50 ppm. Strong coupling between the nuclei is observed on the order of 500 Hz (Figure 2).

Single crystals can be grown from concentrated acetonitrile or dichloromethane solutions and single crystal X-ray diffraction analysis reveals that [dppeP][Br] has an ion-separated structure with two formula units present in the asymmetric unit (Figure 4). The bromide ion may be exchanged for a less reactive anion, such as trifluoromethane sulfonate (triflate, OTf) or tetraphenylborate (BPh<sub>4</sub>). The  $^{31}\text{P}$  NMR spectrum of this product is almost identical to that of the starting material [dppeP][Br] (Figure 3).

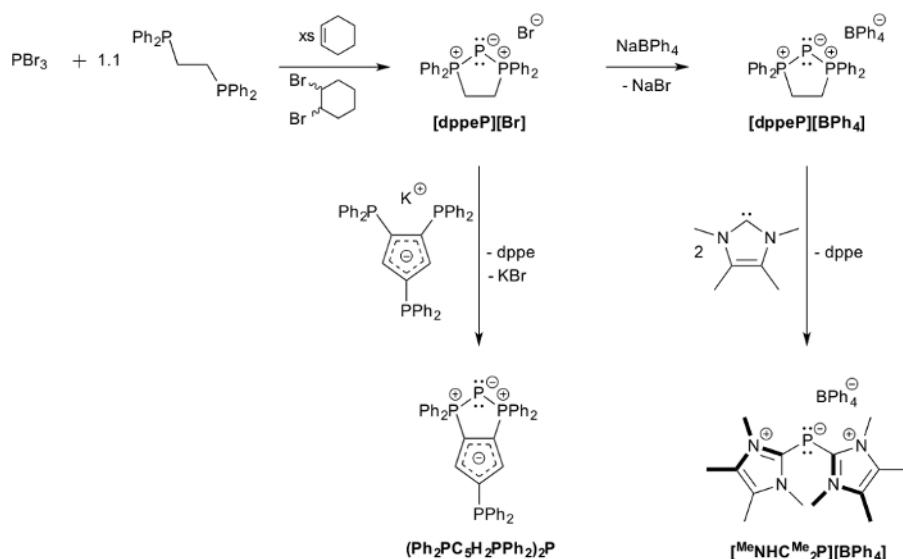
Addition of [dppeP][BPh<sub>4</sub>] to a solution containing two equivalents of the carbene <sup>Me</sup>NHC<sup>Me</sup> results in displacement of the chelating bis-phosphine by the more strongly donating NHC ligands and generates the yellow phosphamethine cyanine dye [<sup>Me</sup>NHC<sup>Me</sup><sub>2</sub>P][BPh<sub>4</sub>] (Figure 1). Because [<sup>Me</sup>NHC<sup>Me</sup><sub>2</sub>P][BPh<sub>4</sub>] is soluble in THF but insoluble in diethyl ether, the latter is used to remove the bisphosphine byproduct, which is highly soluble in most solvents. Once separated by filtration, washed and dried, [<sup>Me</sup>NHC<sup>Me</sup><sub>2</sub>P][BPh<sub>4</sub>] is obtained as an analytically pure yellow powder. The  $^{31}\text{P}$  NMR spectrum of this material dissolved in acetonitrile-d<sub>3</sub> features a singlet signal at -113 ppm, which is significantly shielded relative

to typical phosphalkenes (cf.  $^{31}\text{P}$  NMR  $\delta$  for *P*-mesityldiphenylmethylenephosphine = 233.06 ppm<sup>14</sup>) which is consistent with the phosphorus(I) assignment (**Figure 5**).

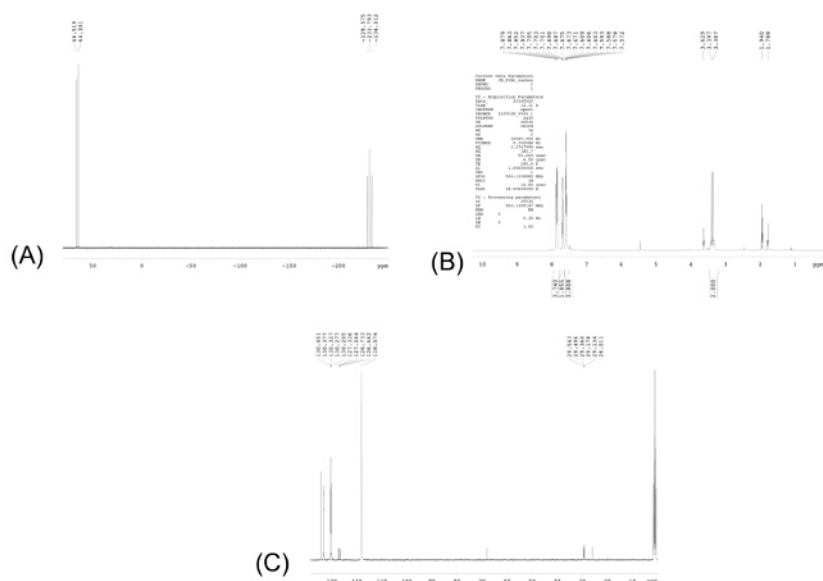
Likewise, the relatively long C-P bond lengths, the acute C-P-C angle and twisting of the heterocycles from the C-P-C plane observed in the crystal structure of  $[\text{MeNHCMe}_2\text{P}][\text{BPh}_4]$  (**Figure 6**) are also most consistent with the phosphorus(I) description. In addition to its potential applications as a dye, compounds such as  $[\text{MeNHCMe}_2\text{P}][\text{BPh}_4]$  have also proven to be useful ligands and reagents for the preparation of cationic phosphines of a type that are useful components in catalytic applications.<sup>15</sup>

The reaction of potassium 1,2,4-tris(diphenylphosphino)cyclopentadiene in a 1:1 stoichiometric ratio with  $[\text{dppeP}][\text{Br}]$  yields  $(\text{Ph}_2\text{P})\text{C}_5\text{H}_2(\text{Ph}_2\text{P})_2\text{P}$  in quantitative yield (**Figure 1**)<sup>9</sup>. The only byproducts from this reaction, namely KBr and dppe, can be removed by filtrations in THF and diethyl ether/pentane respectively. The  $^{31}\text{P}$  NMR spectrum obtained from a concentrated solution of  $(\text{Ph}_2\text{P})\text{C}_5\text{H}_2(\text{Ph}_2\text{P})_2\text{P}$  in  $\text{CD}_2\text{Cl}_2$  (**Figure 7**) reveals the presence of a triplet signal at -174 ppm, attributable to the dicoordinate phosphorus(I) center, a singlet signal at -16.9 ppm for the  $\text{Ph}_2\text{P}$  fragment on the backbone, and a doublet signal attributable to the two  $\text{Ph}_2\text{P}$  groups that chelate the phosphorus(I) center.

This structure of this molecule obtained from a single crystal X-ray diffraction analysis is shown in **Figure 8**. Crystals can be grown via slow evaporation of a concentrated solution of DCM, THF, or even a dilute solution of diethyl ether. The ligand chemistry of  $(\text{Ph}_2\text{P})\text{C}_5\text{H}_2(\text{Ph}_2\text{P})_2\text{P}$  is of interest because the molecule features three different types of donor sites with which it may interact with metals: it features a phosphine site, a phosphide-like site, and a cyclopentadienide site.<sup>9</sup>



**Figure 1.** Reaction of dppe with  $\text{PBr}_3$  and cyclohexene,  $[\text{dppeP}][\text{BPh}_4]$  with  $[\text{MeNHCMe}_2\text{P}][\text{BPh}_4]$ , and  $[\text{dppeP}][\text{Br}]$  with  $[\text{K}][(\text{Ph}_2\text{P})_3\text{C}_5\text{H}_2]$ . [Please click here to view a larger version of this figure.](#)



**Figure 2.**  $^{31}\text{P}$  (A),  $^1\text{H}$  (B), and  $^{13}\text{C}$  (C) NMR spectra of  $[\text{dppeP}][\text{Br}]$  collected in  $\text{CD}_2\text{Cl}_2$  prepared as described in the protocol. [Please click here to view a larger version of this figure.](#)



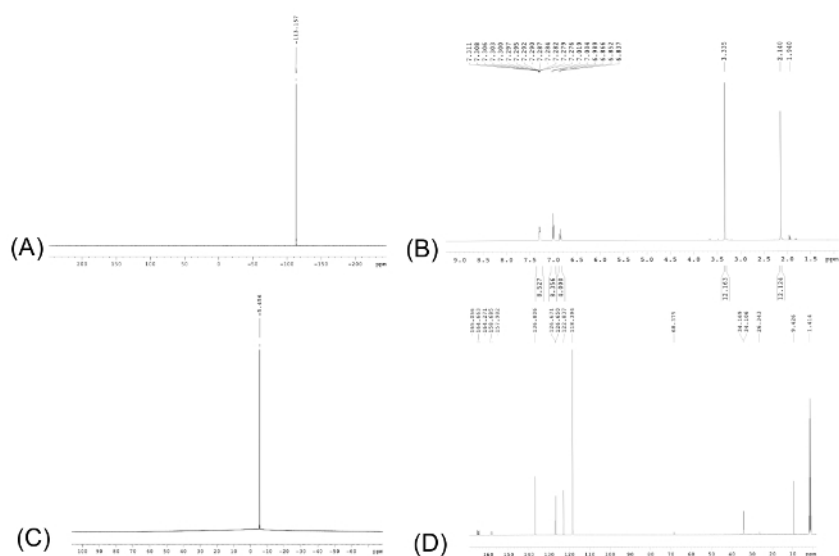


Figure 5.  $^{31}\text{P}$  (A),  $^1\text{H}$  (B),  $^{11}\text{B}$  (C) and  $^{13}\text{C}$  (D) NMR spectra of  $[\text{MeNHCMe}_2\text{P}][\text{BPh}_4]$  collected in  $\text{CD}_3\text{CN}$  prepared as described in the protocol. [Please click here to view a larger version of this figure.](#)

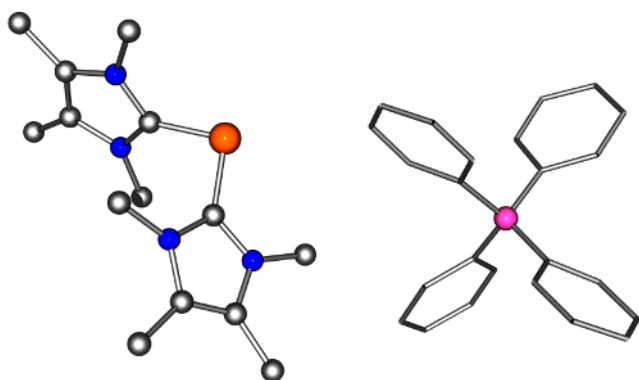


Figure 6. Molecular Structure of  $[\text{MeNHCMe}_2\text{P}][\text{BPh}_4]$ . [Please click here to view a larger version of this figure.](#)

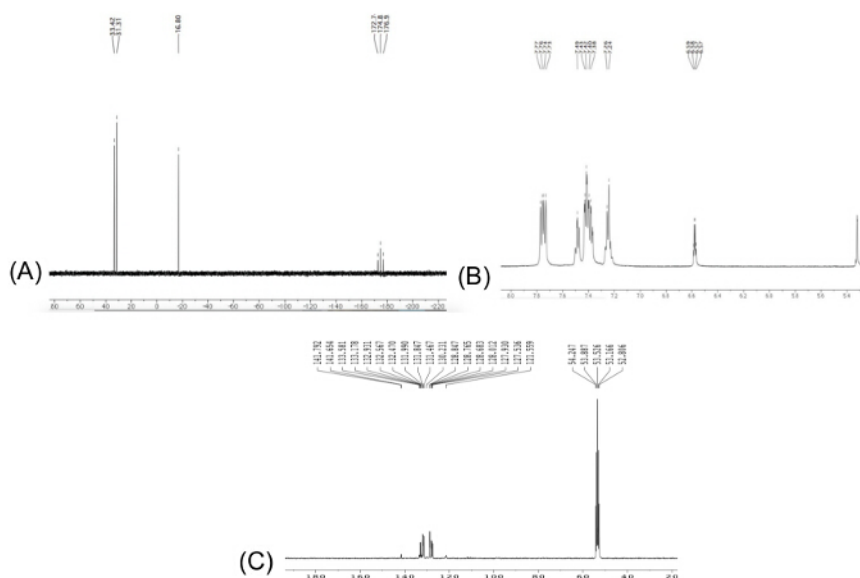
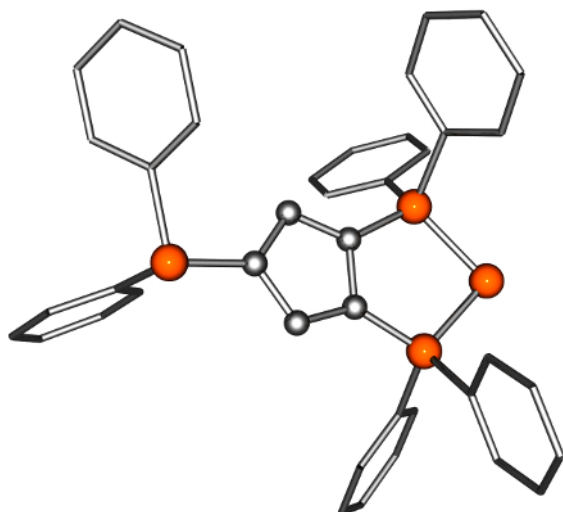


Figure 7.  $^{31}\text{P}$  (A),  $^1\text{H}$  (B), and  $^{13}\text{C}$  (C) NMR spectra of  $(\text{Ph}_2\text{P})\text{C}_5\text{H}_2(\text{Ph}_2\text{P})_2\text{P}$  collected in  $\text{CD}_2\text{Cl}_2$  prepared as described in the protocol. [Please click here to view a larger version of this figure.](#)



**Figure 8. Molecular Structure of  $(\text{Ph}_2\text{P})\text{C}_5\text{H}_2(\text{Ph}_2\text{P})_2\text{P}$ .** Please click here to view a larger version of this figure.

## Discussion

Crystal structures and multi-nuclear NMR ( $^{31}\text{P}$ ,  $^1\text{H}$ , and  $^{13}\text{C}$ ) were obtained for all products reported to confirm connectivity. Electrospray-ionization mass spectrometry was used to confirm presence of the cations and elemental analysis was used to confirm analytical purity of the samples.

It is imperative that all reactions are done in an air-free and dry environment to ensure that no unexpected by-products or decomposition products are formed. Using a slight excess of dppe as well as an excess (10 equivalents) of cyclohexene is necessary, to ensure good yields of  $[\text{dppeP}][\text{Br}]$ .

There are no major limitations of the techniques described herein. The ligand displacement reactions with  $[\text{dppeP}][\text{Br}]$  are only limited to ligands of sufficient donor ability to displace the dppe from the  $[\text{dppeP}][\text{Br}]$  molecule. Notwithstanding, the significant advantage to this methodology is the controlled release of "P" without the generation of unanticipated by-products or the use of harsh reagents. Thus, this methodology can be employed in the future to generate novel molecules containing  $\text{P}^{\text{I}}$  moieties.

## Disclosures

The authors have nothing to disclose.

## Acknowledgements

The authors thank the Natural Sciences and Engineering Research Council (NSERC) of Canada and the Canada Foundation for Innovation (CFI) for funding and scholarship support.

## References

- Macdonald, C. L. B., Ellis, B. D., & Swidan, A. Low-Oxidation-State Main Group Compounds. *Encyclopedia of Inorganic and Bioinorganic Chemistry*. (2011).
- Coffer (née Monks), P. K., & Dillon, K. B. Cyclic triphosphenium ions and related species. *Coord. Chem. Rev.* **257** (5-6), 910-923 (2013).
- Schmidpeter, A., & Lochschmidt, S. New Products from  $\text{PCl}_3$ ,  $\text{P}(\text{NMe}_2)_3$ , and  $\text{AlCl}_3$ . *Angew. Chem. Internat. Ed. in Engl.* **25** (3), 253-254 (1986).
- Schmidpeter, A., Lochschmidt, S., Karaghiosoff, K., & Sheldrick, W. S. Triphosphane-1,3-di-ium Ions. *J. Chem. Soc. Chem. Commun.*, 1447-1448 (1985).
- Ellis, B. D., Carlesimo, M., & Macdonald, C. L. B. Stabilised phosphorus(I) and arsenic(I) iodide: readily-synthesised reagents for low oxidation state main group chemistry. *Chem. Commun.* (15), 1946-1947 (2003).
- Norton, E. L., Szekeley, K. L. S., Dube, J. W., Bomben, P. G., & Macdonald, C. L. B. A convenient preparative method for cyclic triphosphenium bromide and chloride salts. *Inorg. Chem.* **47** (3), 1196-1203 (2008).
- Ellis, B. D., & Macdonald, C. L. B. Phosphorus(I) iodide: a versatile metathesis reagent for the synthesis of low oxidation state phosphorus compounds. *Inorg. Chem.* **45** (17), 6864-74 (2006).
- Kosnik, S. C., Farrar, G. J., Norton, E. L., Cooper, B. F. T., Ellis, B. D., & Macdonald, C. L. B. Low-Valent Chemistry: An Alternative Approach to Phosphorus-Containing Oligomers. *Inorg. Chem.* **11** (53), 13061-13069 (2014).
- Kosnik, S. C., & Macdonald, C. L. B. A zwitterionic triphosphenium compound as a tunable multifunctional donor. *Dalton Trans.* **45** (14), 6251-6258 (2016).

10. Binder, J. F., Swidan, A., Tang, M., Nguyen, J. H., & Macdonald, C. L. B. Remarkably stable chelating bis-N-heterocyclic carbene adducts of phosphorus(I) cations. *Chem. Commun.* **51** (36), 7741-7744 (2015).
11. Binder, J. F., Corrente, A. M., & Macdonald, C. L. B. A simple route to phosphamethine cyanines from S,N-heterocyclic carbenes. *Dalton Trans.* **45** (5), 2138-2147 (2016).
12. Pangborn, A. B., Giardello, M. a., Grubbs, R. H., Rosen, R. K., & Timmers, F. J. Safe and Convenient Procedure for Solvent Purification. *Organometallics*. **15** (5), 1518-1520 (1996).
13. Smaliy, R. V., Beaupérin, M., *et al.* Hexaphosphine: A multifaceted ligand for transition metal coordination. *Eur. J. Inorg. Chem.* (9), 1347-1352 (2012).
14. Klebach, T. C., Lourens, R., & Bickelhaupt, F. Synthesis of mesityldiphenylmethylenephosphine: a stable compound with a localized phosphorus:carbon bond. *J. Amer. Chem. Soc.* **100** (15), 4886-4888 (1978).
15. Alcarazo, M.  $\alpha$ -Cationic Phosphines: Synthesis and Applications. *Chem. Eur. J.* **20** (26), 7868-7877 (2014).