

A Convenient Preparative Method for Cyclic Triphosphenium Bromide and Chloride Salts

Erin L. Norton, Kara L. S. Szekely, Jonathan W. Dube, Paolo G. Bomben, and Charles L. B. Macdonald*

Department of Chemistry and Biochemistry, University of Windsor, Windsor, ON, N9B 3P4, Canada

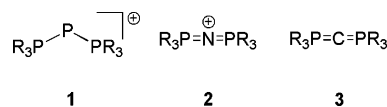
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Analytically pure chloride and bromide salts of two different cyclic triphosphenium cations are prepared by the reaction of PX_3 ($X = Cl, Br$) in the presence of the halogen-scavenging reagent cyclohexene. For the brominated species, the neutral, volatile 1,2-dibromocyclohexane byproduct is readily removed under reduced pressure, and the desired salts are obtained in high yield. Reactions involving phosphorus trichloride are complicated by the formation of salts containing both chloride and hydrogen dichloride anions. Reactivity experiments on potential undesired halogenated diphosphine byproducts suggest that the formation of such species can be prevented by increasing the concentration of cyclohexene employed in the reaction.

Introduction

The chemistry of compounds containing main group elements in unusually low oxidation states (or perhaps more appropriately valence states)¹ has been an area of intense investigation over the last two decades.² Such compounds are of both fundamental and practical interest in comparison to their normal oxidation state counterparts because of the differences in the structural features that are observed, the electronic structures that are adopted, and, most importantly, the unique reactivity patterns engendered by the presence of the unusually electron-rich centers present in such molecules. Whereas much of the research into the lower oxidation state compounds containing the heavier elements of group 15 (pnictogens, $Pn = P, As, Sb, Bi$) has focused on the transient pnictinidenes of the form $R-Pn$ and their related precursor molecules, there has also been considerable interest in stable compounds containing Pn^I centers.^{3–7} In particular, the seminal work in the 1980s of Schmidpeter

demonstrated that triphosphenium cations **1**, which contain P^I centers, are stable compounds that can be readily isolated in many instances.⁸ Triphosphenium cations contain an electron-rich, dicoordinate phosphorus center and are isovalent with bis(phosphine)iminium (PNP) cations **2** and neutral carbodiphosphoranes **3**.⁹ The latter are topical molecules^{10–12} that are related to triphosphenium cations by the diagonal relationship.¹³



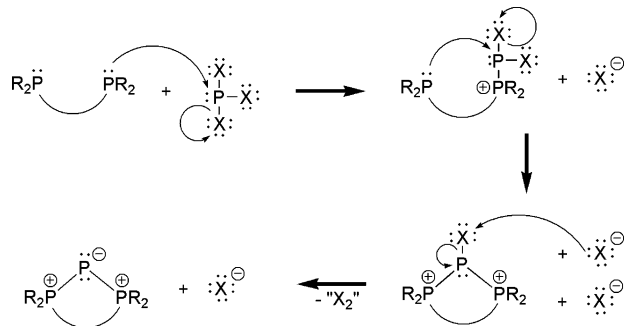
More recently, the research groups of Dillon^{14–16} and Woollins,¹⁷ in addition to our group,¹⁸ have investigated

* To whom correspondence should be addressed. E-mail: cmacd@uwindsor.ca. Phone: (519) 253-3000 ext. 3991. Fax: (519) 973-7098.

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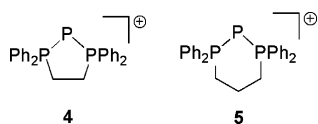
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Scheme 1. Dillon and Monks' Mechanism of Triphosphenium Cation Formation Where X = Cl or Br; the Rate-Determining Step Is the Redox Step Involving the Formal Elimination of X₂ from the P^{III}-Containing Dication Intermediate (Adapted from Ref 23)



synthetic approaches to halide salts of triphosphenium cations¹⁹ (and some of the analogues containing dicoordinate arsenic atoms^{15,18,20–22}). Whereas we were able to demonstrate that the direct reaction of chelating diphosphines with PI₃ in dichloromethane results cleanly in the formation of triphosphenium iodide salts with the concomitant elimination of I₂,¹⁹ the corresponding reactions of PCl₃ or PBr₃ generate significant byproducts in addition to the desired salts under similar conditions.¹⁴ An elegant ³¹P NMR study by Dillon and Monks has recently elucidated the mechanism of the formation of triphosphenium cations under such conditions,²³ as illustrated in Scheme 1, and has demonstrated that the rate-determining step of the reaction is the formal elimination of X₂ (and consequent reduction of the P^{III} center to a P^I center), which rapidly oxidizes the diphosphine ligand to generate the undesirable byproducts. The presence of such byproducts, which are difficult to separate from the desired products because of their similar solubilities, renders the isolation of pure products difficult or impossible and complicates the interpretation of reactivity studies on the triphosphenium halide salts.

In this work, we present a simple synthetic approach that allows for the preparation and isolation of high-purity bromide and chloride salts of some cyclic triphosphenium cations (**4** and **5**). Furthermore, we detail experimental evidence that provides some insight into the nature of the process underlying the formation of the cations and byproducts using this new protocol.



Experimental Section

Reagents and General Procedures. All of the manipulations were carried out using standard inert atmosphere techniques. Phosphorus(III) bromide, phosphorus(III) chloride, 1,2-bis(diphe-

nylphosphino)ethane (dppe), and 1,3-bis(diphenylphosphino)propane (dppp) were purchased from Strem Chemicals Inc., and all of the other chemicals and reagents were obtained from Aldrich; phosphorus(III) bromide and phosphorus(III) chloride were distilled before use, and all of the other reagents were used without further purification. All of the solvents were dried on a series of Grubbs'-type columns²⁴ and were degassed prior to use. CDCl₃ was dried over calcium hydride.

Instrumentation. NMR spectra were recorded at room temperature in CDCl₃ solutions on a Bruker Avance 300-MHz spectrometer. Chemical shifts are reported in ppm, relative to external standards (SiMe₄ for ¹H and ¹³C NMR, 85% H₃PO₄ for ³¹P NMR). Coupling constant magnitudes, |J|, are given in hertz. Melting point (Mp) or decomposition points (Dp) were obtained on samples sealed in glass capillaries under dry N₂ using an Electrothermal melting point apparatus. High-resolution mass spectrometry was performed at the McMaster Regional Centre for Mass Spectrometry. Elemental analyses were performed either at Guelph Chemical Laboratories, Atlantic Microlabs, or in the Centre for Catalysis and Materials Research (CCMR) at the University of Windsor.

Preparation of [(dppe)P][Br] (4**[Br]).** To a colorless solution of PBr₃ (531 mg, 1.961mmol) in CH₂Cl₂ (35 mL) was added cyclohexene (0.62 mL, 6.080mmol) followed by the addition of a colorless solution of dppe (1.641 g, 4.119mmol) in CH₂Cl₂. The colorless solution was stirred at room temperature overnight, after which the white precipitate was filtered and volatile components were removed under reduced pressure. THF (30 mL) was added to the resulting white foam, and the heterogeneous mixture was sonicated at room temperature for 1 h. The solid was then washed with THF (3 × 20 mL) and any remaining volatile components were removed under reduced pressure. The resultant white powder was dissolved in MeCN and after slow evaporation of the solvent a colorless crystalline material was obtained. Yield: 96% (873 mg, 1.172mmol). ³¹P{¹H} NMR: -229.8 (t, ¹J_{PP} = 449, 1P), 64.2 (d, ¹J_{PP} = 449, 2P). ¹³C{¹H} NMR: 30.1 (d, ¹J_{CP} = 44), 126.2 (dd, ¹J_{CP} = 73, ²J_{CP} = 9), 129.8 (t, ²J_{CP} = 6), 132.4 (s), 133.5 (s). ¹H NMR: 3.70 (d, ²J_{HP} = 16, 4H), 7.56 (m, 12H), 7.84 (m, 8H). Dp: 203–206 °C. HRMS (ESI) Calcd for C₂₆H₂₄P₃⁺ 429.1091, found 429.1082 (-2.1 ppm). While we have been unable as of yet to obtain satisfactory microanalytical data for **4**[Br], multinuclear NMR and powder X-ray diffraction experiments suggest that the product is pure.

Preparation of [(dppp)P][Br] (5**[Br]).** To a colorless solution of PBr₃ (415 mg, 1.533mmol) in CH₂Cl₂ (30 mL) was added cyclohexene (0.46 mL, 4.59mmol) followed by the addition of a colorless solution of dppp (905 mg, 2.195mmol). The colorless solution was stirred at room temperature overnight and then filtered, and volatile components were removed under reduced pressure. THF (35 mL) was added to the resulting white foam and the heterogeneous mixture was sonicated at room temperature for 1 h. The solid was then washed with THF (3 × 20 mL) and any remaining volatile components were removed under reduced pressure. The resultant white powder was dissolved in MeCN and after slow evaporation of the solvent a colorless crystalline material was obtained. Yield: 83% (666 mg, 1.273mmol). ³¹P{¹H} NMR: -209.3 (t, ¹J_{PP} = 422, 1P), 23.1 (d, ¹J_{PP} = 422, 2P). ¹³C{¹H} NMR: 19.4 (s), 25.1 (d, ¹J_{CP} = 47), 126.1 (dd, ¹J_{CP} = 75, ²J_{CP} = 8), 129.7 (t, ²J_{CP} = 6). ¹H NMR: 2.74 (m, 2H), 3.34 (m, 4H), 7.50 (m, 12H), 7.75 (m, 8H). Dp : 192–194 °C. HRMS (ESI) Calcd

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Table 1. Summary of X-ray Crystallographic Data for Compounds **4**[Br], **5**[Br], and **5**[HCl₂]

compound	[(dppe)P][Br]	[(dppp)P][Br]	[(dppp)P][HCl ₂]
empirical formula	C ₂₆ H ₂₄ BrP ₃	C ₂₇ H ₂₆ BrP ₃	C ₂₇ H ₂₇ Cl ₂ P ₃
formula weight	509.27	523.30	515.30
temperature (K)	173(2)	173(2)	173(2)
wavelength (Å)	0.71073	0.71073	0.71073
habit, color	prism, colorless	prism, colorless	prism, colorless
crystal system	triclinic	monoclinic	monoclinic
space group	P1	P2 ₁ /c	P2 ₁ /n
unit cell dimensions:			
<i>a</i> (Å)	9.8923(17)	11.1018(11)	12.594(2)
<i>b</i> (Å)	13.499(2)	18.9235(19)	16.088(3)
<i>c</i> (Å)	19.672(4)	12.9372(13)	12.686(2)
α (deg)	71.401(2)	90	90
β (deg)	79.610(2)	113.898(1)	91.516(2)
γ (deg)	69.134(2)	90	90
volume (Å ³)	2319.9(7)	2484.9(4)	2569.3(8)
<i>Z</i>	4	4	4
density (calculated) (g cm ⁻³)	1.458	1.399	1.332
absorption coefficient (mm ⁻¹)	1.990	1.860	0.454
<i>F</i> (000)	1040	1072	1072
θ range for data collection (deg)	1.10 to 27.50	2.01 to 27.50	2.04 to 27.50
limiting indices	-12 ≤ <i>h</i> ≤ 12, -17 ≤ <i>k</i> ≤ 17, -25 ≤ <i>l</i> ≤ 24	-14 ≤ <i>h</i> ≤ 14, -21 ≤ <i>k</i> ≤ 24, -16 ≤ <i>l</i> ≤ 16	-15 ≤ <i>h</i> ≤ 16, -20 ≤ <i>k</i> ≤ 20, -16 ≤ <i>l</i> ≤ 16
reflns collected	26 158	20 497	21 165
independent reflns	10 287	5614	5770
<i>R</i> _{int}	0.0259	0.0536	0.0435
absorption correction	SADABS	SADABS	SADABS
refinement method	refinement method	full matrix least-squares on <i>F</i> ²	
data/restraints/params	10 287/0/541	5614/0/280	5770/0/293
GOF on <i>F</i> ²	1.048	1.033	1.032
Final <i>R</i> indices ^a [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> 1 = 0.0348, <i>wR</i> 2 = 0.0812	<i>R</i> 1 = 0.0471, <i>wR</i> 2 = 0.0886	<i>R</i> 1 = 0.0410, <i>wR</i> 2 = 0.0912
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0496, <i>wR</i> 2 = 0.0943	<i>R</i> 1 = 0.0758, <i>wR</i> 2 = 0.0996	<i>R</i> 1 = 0.0604, <i>wR</i> 2 = 0.0997
largest difference map peak and hole (e Å ⁻³)	0.654 and -0.299	0.591 and -0.301	0.434 and -0.313

^a $R_1(F) = \sum(|F_o| - |F_c|)/\sum|F_o|$ for reflections with $F_o > 4(\sigma(F_o))$. $wR_2(F^2) = \{\sum w(|F_o|^2 - |F_c|^2)^2/\sum w(|F_o|^2)^2\}^{1/2}$, where *w* is the weight given each reflection.

Table 2. Selected Metrical Parameters for Compounds **4**[Br], **5**[Br], and **5**[HCl₂]^a

	[(dppe)P][Br]	[(dppp)P][Br]	[(dppp)P][HCl ₂]
P1–P2	2.1231(9) [2.1216(9)]	2.1138(11)	2.1254(8)
P2–P3	2.1308(9) [2.1270(9)]	2.1262(11)	2.1132(8)
P1–C5 (or –C6)	1.818(2) [1.820(2)]	1.801(3)	1.811(2)
P3–C4	1.817(2) [1.836(2)]	1.807(3)	1.814(2)
C4–C5	1.525(3) [1.523(3)]	1.525(4)	1.531(3)
C5–C6		1.538(4)	1.530(3)
P1–P2–P3	88.37(3) [89.17(3)]	98.30(4)	96.70(3)

^a Distances are reported in angstroms and angles in degrees; for **4**[Br], the corresponding values for each independent cation in the asymmetric unit are reported separately.

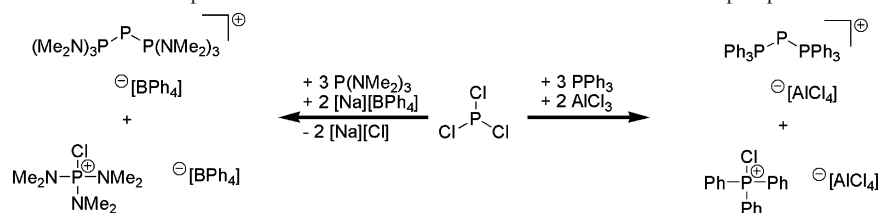
for C₂₇H₂₆P₃⁺ 443.1247, found 443.1269 (+4.9 ppm). Anal. Calcd For C₂₇H₂₄BrP₃ (523.321): C 61.97, H 5.01. Found: C 62.24, H 5.31.

Preparation of [(dppe)P][Cl] (4**[Cl]).** To a colorless solution of PCl₃ (500 mg, 3.64mmol) in CH₂Cl₂ (30 mL) was added cyclohexene (1.1 mL, 10.9mmol) followed by the addition of a colorless solution of dppe (1.89 g, 4.73mmol). The colorless solution was stirred at room temperature overnight and then filtered, and volatile components were removed under reduced pressure. THF (35 mL) was added to the resulting white foam and the heterogeneous mixture was sonicated at room temperature for 1 h. The solid was then washed with THF (3 × 20 mL) and any remaining volatile components were removed under reduced pressure. The crude white powder was dissolved in a minimal amount of CH₂Cl₂ and after the precipitation of a yellow byproduct, the solution was filtered

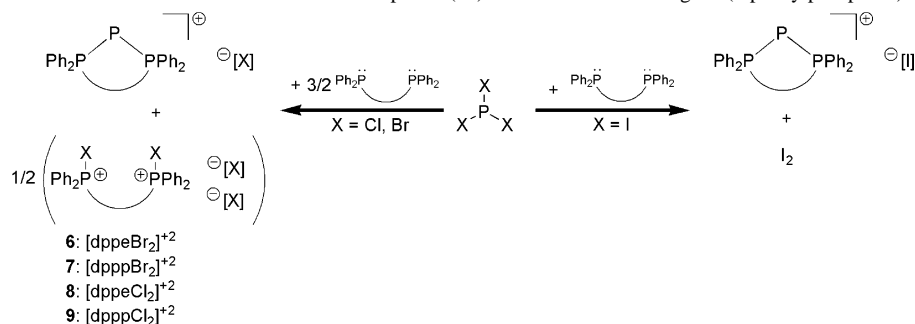
and all of the remaining volatile components were removed under reduced pressure. The resultant white powder was dissolved in MeCN and after slow evaporation of the solvent a colorless crystalline material was obtained. Yield: 56% (948 mg, 2.04mmol). ³¹P{¹H} NMR: -228.9 (t, ¹J_{PP} = 448, 1P), 64.6 (d, ¹J_{PP} = 448, 2P). ¹³C{¹H} NMR: 29.9 (d, ¹J_{CP} = 44), 126.2 (dd, ¹J_{CP} = 75, ²J_{CP} = 8), 129.7 (t, ²J_{CP} = 6), 132.3 (s), 133.4 (s). ¹H NMR: 3.75 (d, ²J_{HP} = 16, 4H), 7.57 (m, 12H), 7.86 (m, 8H). Dp : 90–91 °C. HRMS (ESI) Calcd for C₂₆H₂₄P₃⁺ 429.1091, found 429.1099 (+1.9 ppm). Anal. Calcd For C₂₆H₂₄ClP₃ (468.843): C 67.18, H 5.20. Found: C 67.07, H 4.84.

Preparation of [(dppp)P][Cl] (5**[Cl]).** To a colorless solution of PCl₃ (210 mg, 1.53mmol) in CH₂Cl₂ (30 mL) was added cyclohexene (0.44 mL, 4.39mmol) followed by the addition of a colorless solution of dppp (780 mg, 1.89mmol). The colorless solution was stirred at room temperature overnight and then filtered, and volatile components were removed under reduced pressure. THF (35 mL) was added to the resulting white foam and the heterogeneous mixture was sonicated at room temperature for 1 h. The solid was then washed with THF (3 × 20 mL) and any remaining volatile components were removed under reduced pressure. The crude white powder was dissolved in a minimal amount of CH₂Cl₂ and after the precipitation of a yellow byproduct, the solution was filtered and all of the remaining volatile components were removed under reduced pressure. The resultant white powder was dissolved in MeCN and after slow evaporation of the solvent a colorless crystalline material was obtained. Yield: 45% (345 mg, 0.72mmol). ³¹P{¹H} NMR: -209.4 (t, ¹J_{PP} = 422, 1P),

Scheme 2. Some Early Reactions of Schmidpeter et al. Consistent with the Intermediate Formation of Triphosphenium Chloride Salts



Scheme 3 Differing Behaviors Observed for the Reactions of Phosphorus(III) Halides with Chelating Bis(diphenylphosphino)alkane Ligands^a



^a Only one of the potential halophosphonium products is included.

23.1 (d, ¹J_{PP} = 422, 2P). ¹³C{¹H} NMR: 19.3 (s), 25.1 (d, ¹J_{CP} = 47), 125.9 (dd, ¹J_{CP} = 75, ²J_{CP} = 10), 129.7 (t, ²J_{CP} = 6), 132.3 (s), 133.4 (s). ¹H NMR: 2.72 (m, 2H), 3.29 (m, 4H), 7.45 (m, 12H), 7.75 (m, 8H). Dp: 140–141 °C. HRMS (ESI) Calcd for C₂₇H₂₆P₃⁺ 443.1247, found 443.1252 (+1.0 ppm). Anal. Calcd For C₂₇H₂₆-ClP₃ (478.869): C 67.72, H 5.47. Found: C 67.54, H 5.74.

Small-Scale Preparation and ³¹P NMR Spectroscopic Identification of the Cations in [dppeBr₂][A]₂ (6[A]₂) and [dpppBr₂][A]₂ (7[A]₂); A = Br or Br₃. An excess of liquid Br₂ was added to dichloromethane solutions of either dppe or dppp and stirred for several hours. All of the volatile components were removed under reduced pressure and the resultant solids were dissolved in CDCl₃. ³¹P{¹H} NMR: **6** 60.1(s); **7** 61.6(s).

Small-Scale Preparation and ³¹P NMR Spectroscopic Identification of the Cations in [dppeCl₂][A]₂ (8[A]₂) and [dpppCl₂][A]₂ (9[A]₂); A = Cl or Cl₃. Pure Cl₂ gas was bubbled through dichloromethane solutions of either dppe or dppp until the solutions retained the yellow-green color. All of the volatile components were removed under reduced pressure and the resultant solids were dissolved in CDCl₃. ³¹P{¹H} NMR: **8** 75.2(s); **9** 75.8(s).

Preparation of [dppeBr₂][Br₃]₂ (6[Br₃]₂). To a colorless solution of dppe (1.97 g, 4.94mmol) in CH₂Cl₂ was added Br₂ (0.51 mL, 9.89mmol) dropwise until a bright yellow color persisted. The solution was stirred at room temperature for 20 min before a white precipitate formed. The reaction mixture was stirred overnight after which the yellow solution was separation from the white solid. All of the volatile components remaining were removed and the white solid was collected. All of the attempts at recrystallization were unsuccessful because of the amorphous nature of the compound, as confirmed by powder X-ray diffraction experiments. Yield: 55.5% (2.85 g, 2.74mmol). ³¹P{¹H} NMR: 60.1(s). ¹³C{¹H} NMR: 25.2 (m), 117.7 (m), 130.8 (s), 134.0 (s), 136.9 (s). ¹H NMR: 4.64 (s, 4H), 7.80 (m, 12H), 8.35 (m, 8H). Mp: 128–132 °C.

Preparation of [dppeBr₂][Br]₂ (6[Br]₂) from 6[Br₃]₂. To a yellow solution of 6[Br₃]₂ (200 mg, 0.21mmol) in a 4:1 mixture of CH₂Cl₂ and CHCl₃ (25 mL) was added cyclohexene (110μL, 1.08mmol, 5.15equiv.) giving rise to a lighter yellow solution. Following 3 h of stirring, the reaction mixture of the volatile components were removed under reduced pressure and a light gray

powder was collected. Yield: 56% (77 mg, 0.12mmol). ³¹P{¹H} NMR: 58.2(s). ¹³C{¹H} NMR: 21.7 (m), 122.1 (m), 130.5 (s), 132.0 (s), 135.3 (s). ¹H NMR: 3.56 (s, 4H), 7.67 (m, 12H), 8.05 (m, 8H). Mp: 187–190 °C.

We have been as yet unable to obtain a satisfactory microanalysis for compounds **6**[Br₃]₂ and **6**[Br]₂; please note that **6**[Br]₂ is a well-known organic reagent that is generally prepared and used in situ.²⁵ Whereas dication **6** is unambiguously identified as the only observed component in both salts by the multinuclear NMR data presented above, the identity of the anions is not provided by such experiments; please see the Supporting Information for data that corroborates our assignment of the anions in each of the salts.

X-ray Crystallography. Each crystal was covered in Nujol and placed rapidly into the cold N₂ stream of the Kryo-Flex low-temperature device. The data were collected using the SMART²⁶ software on a Bruker APEX CCD diffractometer using a graphite monochromator with Mo Kα radiation (λ = 0.71073 Å). A hemisphere of data was collected using counting times of 10–30 s per frame. The data were collected at –100 °C. Details of crystal data, data collection, and structure refinement are listed in Table 1, and selected metrical parameters are compiled in Table 2. Data reductions were performed using the SAINT²⁷ software and the data were corrected for absorption using SADABS.²⁸ The structures were solved by direct methods using SIR97²⁹ and refined by full-matrix least-squares on F² with anisotropic displacement parameters for the non-hydrogen atoms using SHELXL-97³⁰ and the WinGX³¹ software package. Details of the final structure solutions were evaluated using PLATON and thermal ellipsoid plots were produced using SHELXTL.³² Powder X-ray diffraction experiments were performed with a Bruker D8 Discover diffractometer equipped with a Hi-Star area detector using Cu Kα radiation (λ = 1.54186 Å).

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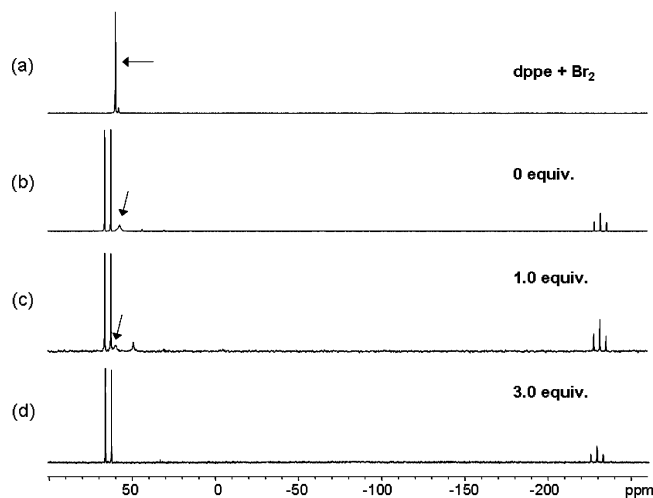


Figure 1. ^{31}P NMR spectra of the reactions of: (a) dppe and excess Br_2 and PBr_3 with dppp in the presence of (b) no cyclohexene, (c) 1 equiv of cyclohexene, and (d) 3 equiv of cyclohexene. The signal corresponding to the dication **6** is indicated with an arrow. Relevant chemical shift assignments: ca. 60 ppm (s, $[\text{dppe}\cdot\text{Br}_2]^{+2}$), 65 ppm (d, $[(\text{dppe})\text{P}]^+$), -230 ppm (t, $[(\text{dppe})\text{P}]^+$), ca. 34 ppm (s, $\text{dppe}\cdot\text{O}_2$).

Results and Discussion

As early as 1985, the research group of Schmidpeter demonstrated that the direct reaction of phosphorus(III) chloride with some phosphine donors can result in the disproportionation of PCl_3 and the generation of triphosphenium salts, as illustrated in Scheme 2.^{33,34} Whereas the parent chloride salts were not isolated, chloride complexation with AlCl_3 provided the salt $[(\text{Ph}_3\text{P})_2\text{P}][\text{AlCl}_4]$,^{33,35} and salt metathesis with $[\text{Na}][\text{BPh}_4]$ was used to obtain the salt $\{-(\text{Me}_2\text{N})_3\text{P}\}_2\text{P}][\text{BPh}_4]$,³⁴ both of these results are consistent with at least the intermediate formation of triphosphenium chloride salts.

More recently, the research group of Dillon investigated the reaction of phosphorus(III) halides with a large variety of monodentate and bidentate phosphine donors using ^{31}P NMR spectroscopy.^{14,15} In addition to the desired salts, the NMR spectra consistently indicated the formation of the oxidized (halogenated) phosphines as byproducts in the reaction mixtures. Unfortunately, the solubility characteristics of the byproducts are very similar to those of the desired triphosphenium salts, which makes separation and purification of the target compounds very difficult. However, we discovered that, under certain conditions, it is possible to generate triphosphenium iodide salts through the diphosphine-assisted disproportionation of PI_3 .^{18,19} When such reactions are performed in non-coordinating solvents, such as dichloromethane, the only phosphorus-containing product is the desired triphosphenium iodide salt and the byproduct is elemental iodine, as illustrated in Scheme 3.

Unfortunately, when the analogous reactions of chelating diphosphines with PCl_3 or PBr_3 are attempted in dichlo-

romethane (also illustrated in Scheme 3), the unwanted and difficult to remove byproducts are generated including: $[\text{dppe}\cdot\text{Br}_2][\text{Br}]_2$, **6** $[\text{Br}]_2$; $[\text{dppp}\cdot\text{Br}_2][\text{Br}]_2$, **7** $[\text{Br}]_2$; $[\text{dppe}\cdot\text{Cl}_2][\text{Cl}]_2$, **8** $[\text{Cl}]_2$; and, $[\text{dppp}\cdot\text{Cl}_2][\text{Cl}]_2$, **9** $[\text{Cl}]_2$. The conventional explanation for the differences in the observed behavior is that the diphosphine reagents are acting as both ligands and reducing agents in the reactions containing the chloro- or bromophosphines but only as ligands in the reaction with PI_3 (at least when it is conducted in dichloromethane).¹⁴ We had postulated that an alternative but related interpretation for this observation is that the larger reduction potentials of intermediately formed Cl_2 and Br_2 in comparison to that of I_2 result in the rapid oxidation of some of the diphosphine ligand and prevents their direct observation.¹⁹ Recently, Dillon and Monks elucidated the mechanism of formation for cyclic triphosphenium cations (which is almost certainly also applicable to acyclic cations) and have suggested that the rate-determining step is the P^{III} to P^{I} redox process in which a formal equivalent of X_2 ($\text{X} = \text{Cl}, \text{Br}$) is removed from the intermediate salt and oxidizes the diphosphine.²³ The reactions are observed to be more rapid for the bromophosphines than for the chlorophosphines; such behavior is consistent with both interpretations of the redox process.

Regardless of the mechanistic details, the formation of byproducts has rendered the isolation of chloride or bromide salts of triphosphenium cations difficult, thus we sought a synthetic approach that would provide the desired salts with fewer or more-conveniently removable byproducts. We reasoned that the ideal byproduct for our purposes would be a neutral, relatively unreactive molecule that is either soluble in nonpolar solvents or, more preferably, readily removed under reduced pressure so that it could be easily separated from the triphosphenium salts. Since we required a molecule that would have these properties and that would formally sequester one equivalent of X_2 ($\text{X} = \text{Cl}, \text{Br}$) from the reaction mixture, cyclohexene, which is a well-known reagent used for the removal of bromine used in organic syntheses,³⁶ appeared to be a potentially reasonable candidate. Furthermore, preliminary ^{31}P , ^1H and ^{13}C NMR investigations revealed that cyclohexene does not react with any of the other reagents (PCl_3 , PBr_3 , dppe, dppp) so its suitability as a halogen-sequestering agent in this system was evaluated.

^{31}P NMR spectra reveal that when a dichloromethane solution containing a mixture of equimolar amounts of cyclohexene and PBr_3 is mixed with a dichloromethane solution containing one equivalent of either of the chelating diphosphines, the desired triphosphenium cation (**4** or **5**) is formed and the relative amount of oxidized product (**6**: δ 60 ppm or **7**: δ 62 ppm) is reduced significantly (ca. 40%) as assessed by integration of the corresponding signals in the spectra, as illustrated in Figure 1. Because some of the bromophosphonium byproduct was still present, several syntheses were attempted with excess amounts of cyclohexene. As shown in Figure 1, when ca. 3 equiv (or more) of

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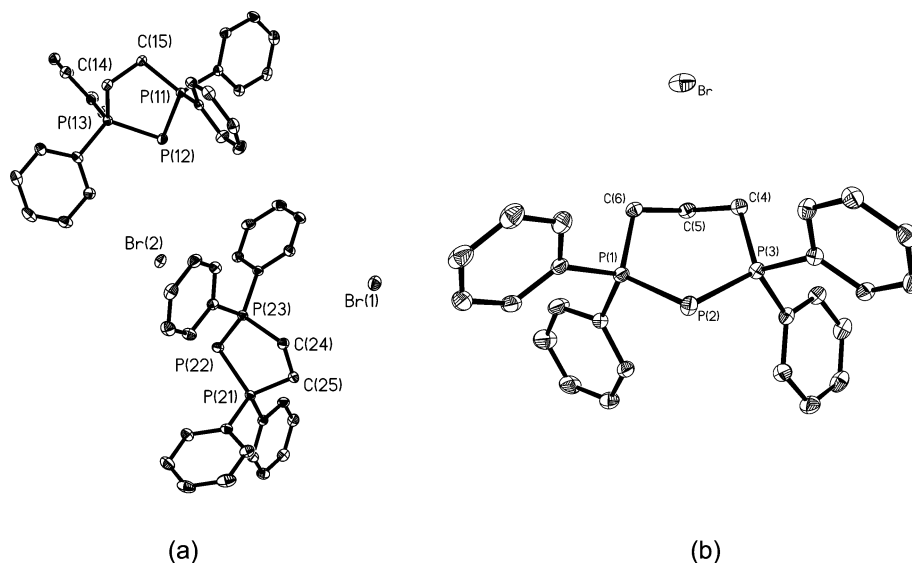


Figure 2. Thermal ellipsoid plots (30% probability surface) of the contents of the asymmetric units of the P^I bromide salts **4**[Br] (a) and **5**[Br] (b). Hydrogen atoms have been removed for clarity.

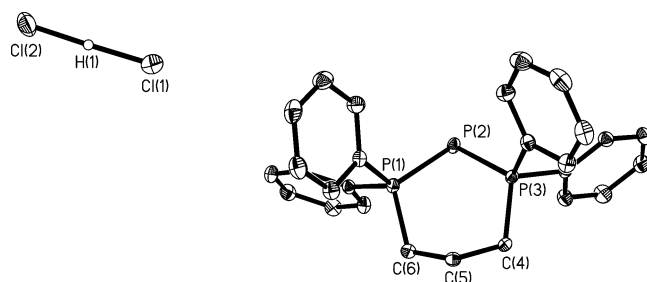


Figure 3. Thermal ellipsoid plot (30% probability surface) of the contents of the asymmetric unit of [(dppp)P][HCl₂], **5**[HCl₂]. Most of the hydrogen atoms have been removed for clarity.

cyclohexene are present in the reaction mixture, there are no longer any peaks attributable to the bromophosphonium byproduct. ¹H NMR and GC-MS experiments on sealed samples confirm the formation of the expected trans-1,2-dibromocyclohexane however, in practice, the byproduct may be conveniently removed with the other volatile components of the reaction mixture under reduced pressure.

While ³¹P NMR spectra suggest that the resultant solid is essentially pure, we have found that the product should be sonicated with THF prior to recrystallization in order to obtain the purest samples of the triphosphenium bromide salts. The slow evaporation of a solution of the cleaned solid in acetonitrile results in the production of crystalline salts characterized as the triphosphenium bromide salts **4**[Br] and **5**[Br]. The identities and purities of these materials have been confirmed in each case by multinuclear NMR experiments, HRMS experiments and microanalyses.

For the bromide salts **4**[Br] and **5**[Br], the recrystallization produced materials suitable for examination by single-crystal X-ray diffraction. Details of the data collection and refinement for the structures are listed in Table 1 and the values of selected metrical parameters are collected in Table 2; the asymmetric unit of each salt is depicted in Figure 2. Perhaps not surprisingly, each of the bromide salts is isostructural with the corresponding iodide salt¹⁹ and, consequently, the

geometrical features of the cations in each structure fall in the ranges (P–P distances: 2.113(2)–2.184(2) Å) found in the Cambridge Structural Database³⁷ for these cyclic triphosphenium cations reported previously^{14,19,38–40} and do not mandate further discussion.

In contrast to the high-yield and clean synthesis observed for the bromide salts, we have found that the corresponding reactions involving PCl₃ are somewhat more complicated. As in the case of the bromide analogues described above, ³¹P NMR experiments confirm the formation of the desired cation; however, the yields of the pure chloride salts are, in every instance, considerably lower than those of the bromine-containing salts. Furthermore, it must be noted that significant washing and fractional recrystallization are necessary to obtain chloride salts of sufficient purity for microanalysis, and the presence of some phosphorus-containing byproducts in the reaction mixtures suggested to us that a more in-depth examination of this system was mandated.

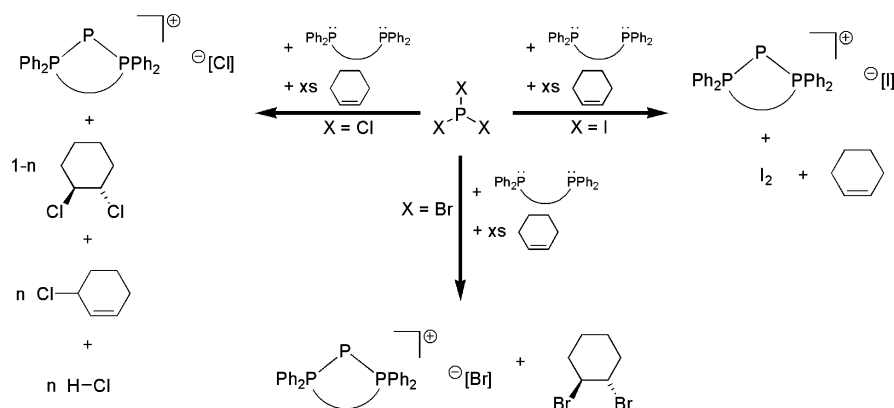
Our suspicions were confirmed upon the examination of the crystal structure of a crystal obtained from the recrystallization of the crude reaction products. As illustrated in Figure 3, the salt that crystallized from the reaction mixture is NOT the anticipated chloride salt but is in fact the hydrogen dichloride salt [(dppp)P][HCl₂], **5**[HCl₂]. The metrical parameters of the cation in the salt are indistinguishable from those found in other salts containing the cation and require no further comment. Similarly, the hydrogen dichloride anion, while relatively rare in terms of the number of examples (15) reported in the CSD, exhibits a Cl–Cl distance of 3.1161(11) Å, Cl–H distances of 1.54(4) and

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Scheme 4. Summary of the Reactions of Phosphorus(III) Halides with Chelating Bis(diphenylphosphino)alkane Ligands in the Presence of Excess Cyclohexene

1.58(4) Å, and a Cl–H–Cl angle of 178(3)°; all of these values are consistent with those that have been previously observed.

It should be indicated that the hydrogen dichloride salt is obtained reproducibly even after the thorough drying and redistillation of all of the reagents and solvents employed in the reaction. We also wish to note that whereas each of the pure halide salts appears to be stable indefinitely to atmospheric conditions in both the solid state and solution phases; dichloromethane or acetonitrile solutions containing mixtures of chloride and hydrogen dichloride salts slowly decompose partially to generate an orange insoluble material. Analytically pure samples of the chloride salts may be obtained by fractional crystallization of the crude products, although the need for such additional workup is less than ideal.

From the foregoing, it is clear that the nature of the products from the reactions outlined above appear to depend on the identity of the halogen used for the source of the P^{I} center. In an effort to understand the behavior observed, we undertook a series of further investigations. Analysis of the components present in the reaction mixtures using GC-MS reveals that, in the cases where $\text{X} = \text{Br}$, the only bromine-containing product identified is trans-1,2-dibromocyclohexane, whereas when $\text{X} = \text{Cl}$ there are several chlorine-containing products including the expected trans-1,2-dichlorocyclohexane as well as 3-chlorocyclohexene. This latter product is instructive in that it is consistent with one of the products observed in the direct reaction of cyclohexene with Cl_2 ^{41,42} and it produces HCl as a byproduct; this HCl can presumably combine with chloride anions present in the reaction mixture to generate the observed $[\text{HCl}_2]^-$ anions.

Because the presence of HCl in the reaction mixture is the most likely source of the hydrogen dichloride anion, we postulated that it might be possible to obtain the chloride salts in higher yield and purity through the use of a base to remove the HCl. To prove this hypothesis, a dilute solution of triethylamine in dichloromethane was added to the reaction mixture after 2 h. After filtration, removal of volatile components, sonication, and recrystallization, the resultant solid exhibited spectroscopic and physical properties identical

to those observed for the analytically pure samples of the chloride salts **4**[Cl] and **5**[Cl], but the yield was not improved tremendously. Attempts at neutralizing the HCl with triethylamine during the reaction created additional phosphorus-containing byproducts and were not pursued further.

Given that the halogenated products derived from the cyclohexene-sequestering agent appeared to be consistent with those observed from the direct reaction of cyclohexene with elemental chlorine or bromine, we wished to ascertain whether the halogenated diphosphine byproducts **6**[A]₂, **7**[A]₂, **8**[A]₂, and **9**[A]₂ (A = the appropriate halide or trihalide anions) also react with cyclohexene; that is, these experiments were undertaken to assess whether the reaction may proceed through the initial oxidation of the diphosphine followed by reaction with cyclohexene or if such an intermediate is unnecessary. To this end, we prepared the halogenated compounds **6**[A]₂, **7**[A]₂, **8**[A]₂, and **9**[A]₂ through the reaction of either dppp or dppp with the elemental halogens. In the case of the brominated compounds, the materials appear to be obtained initially as the yellow-colored tribromide salts (i.e., **6**[Br]₃ and **7**[Br]₃) when an excess of bromine is used. In contrast, we did not find any evidence of trichloride anions when excess chlorine was present.

The treatment of the halogenated diphosphonium species **6**[Br]₂, **7**[Br]₂, **8**[Cl]₂, and **9**[Cl]₂ with cyclohexene does not change the appearance of the ³¹P NMR spectra in chloroform and suggests that these halophosphonium halide salts do not react with cyclohexene. In the case of the tribromide salts **6**[Br]₃ (which we synthesized and characterized more completely) and **7**[Br]₃, we do observe the disappearance of the yellow color upon the addition of cyclohexene. Furthermore, we observe the formation of 1,2-dibromocyclohexane and obtain the corresponding bromide salts as the only phosphorus-containing product. Such behavior suggests that the halophosphonium salts are not effective halogenating agents for cyclohexene; however, the *tribromide anion* is able to effect the halogenation (or alternatively, it suggests that cyclohexene may be a useful reagent for the conversion of tribromide salts to bromide salts).

In light of the foregoing, it appears that dications such as **6**, **7**, **8**, and **9** are not generated (even as intermediates) in the syntheses of the triphosphonium salts when sufficient

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cyclohexene is present. The appearance of some of the halogenated phosphonium species at lower concentrations of cyclohexene suggests that the diphosphine and the olefin are each oxidized readily and rapidly by either free X_2 or, perhaps more likely, the corresponding $[(dppe/p)PX]^{+2}$ intermediate²³ and that it is possible to preclude the formation of the phosphorus-containing byproduct by simply decreasing the probability that a diphosphine versus an olefin will be proximate to the oxidant upon its release of X_2 . In this light, the halogen sequestration strategy we have outlined above is best accomplished using an excess of cyclohexene.

For completeness, it should be noted that no reaction is observed when I_2 is mixed with cyclohexene and, similarly, cyclohexene does not appear to sequester the I_2 that is generated by the reaction of chelating diphosphines with PI_3 . Such behavior is, as one would expect, on the basis of the relative reduction potentials of I_2 versus Br_2 versus Cl_2 and/or on the basis of the relative strengths of the P–X bonds. The results of the reactions observed for the three different phosphorus(III) halides are summarized in Scheme 4.

Conclusions

We have shown that the sequestration of Br_2 using a simple unsaturated organic reagent is a viable method for the production of pure triphosphenium bromide salts. Whereas the approach can also be used to obtain the analogous chloride salts, additional workup and fractional recrystallization are required to obtain pure samples because of the bimodal nature of the chlorination of cyclohexene. Alternatively, the additional use of a base to remove HCl from the reaction mixture may also be used to increase the yield of the pure chloride salts. In light of the observed behavior, we now suggest that the cleanest and easiest method for the generation of cyclic triphosphenium cations in the absence of reactive byproducts is to treat PBr_3 with the desired chelating diphosphine in the presence of an excess of cyclohexene. It is likely that numerous other olefins may be suitable reagents for halogen sequestration, and preliminary spectroscopic results suggest that this approach will also work for certain acyclic triphosphenium salts.

Of perhaps more general importance, it is quite possible that the X_2 -sequestration approach to the generation of low oxidation state compounds will be applicable to related

molecules containing other main group elements. Given that it has now been demonstrated that the ligand-induced reductive elimination of X_2 from higher oxidation state precursors provides superior or unique synthetic routes to, for example *N*-heterocyclic phosphonium and arsenium cations,^{43–47} group 16 heterocycles,^{48–50} phosphamethinecyanine dyes,⁵¹ and other interesting classes of molecules,^{52,53} this new halogen sequestration approach may prove to be a useful addition to the toolkits of synthetic chemists.

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Supporting Information Available: Summary of crystallographic data in CIF format for five compounds and powder X-ray diffraction data for one compound. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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