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# Characterization of Cyclic Triphosphenium Ions in Solution, and the Crystal and Molecular Structure of 1,1,3,3-Tetraphenyl-tetrahydro-1,2,3-triphosphenium Hexachlorostannate.

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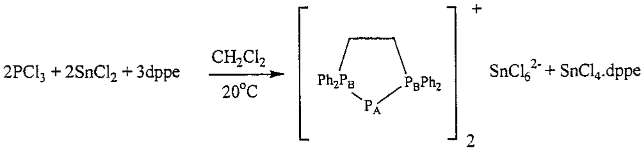
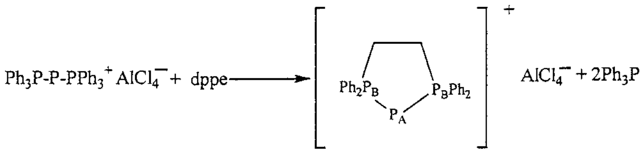
ABSTRACT: *The preparation in solution of a number of cyclic triphosphenium ions and their identification by $^{31}P$ NMR spectroscopy are described; the crystal and molecular structure of the six-membered cationic ring (as its hexachlorostannate) has been determined.* © 2000 John Wiley & Sons, Inc. Heteroatom Chem 11:226–231, 2000

## *INTRODUCTION*

In 1982, Schmidpeter and coworkers described the synthesis and characterization by X-ray crystallography of a five-membered ring cyclic triphosphenium ion (as its hexachlorostannate (IV) salt, with two moles of $CH_2Cl_2$ of solvation) [1]. The preparation was later included in *Inorganic Syntheses,* proceeding according to equation (1) [2]. In this reaction, $SnCl_2$ acts as a reducing agent (and chlorine acceptor). The structure showed that the P–P distances were very similar (2.122(1) and 2.128(2) Å), and shorter than normal P–P single bonds (2.20–2.25 Å) [3], whereas the bond angle at the central phosphorus $P_A$ of 88.9(1)° indicated a high degree of charge delocalization [1]. The $^{31}P$ spectrum of the cation consisted of a doublet at $\delta$ 63.8 ppm for $P_B$, and a triplet for $P_A$ at $\delta$ $-231.6$ ppm, $^1J_{P_AP_B}$ 448.9 Hz, confirming the equivalence of the two $P_B$ atoms. The tetrachloroaluminate salt was subsequently prepared ($\delta$ $P_B$ 64.4, $\delta$ $P_A$ $-232.0$ ppm, $^1J_{P_AP_B}$ 451.5 Hz) according to equation (2), by displacement of $Ph_3P$ from a linear precursor [4].



(dppe = 1,2-*bis*diphenylphosphinoethane) (1)



(2)

The same article contained $^{31}P$ NMR solution data for three other triphosphenium cations with either a five-, six-, or two six-membered rings, each ring having three linked phosphorus atoms [4]. The chemical

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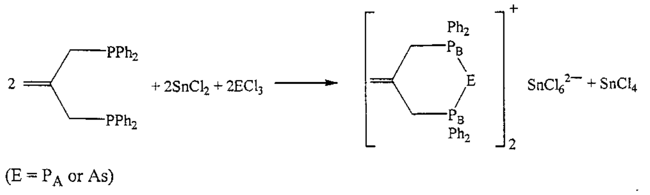
Dedicated to Prof. Alfred Schmidpeter on the occasion of his 70th birthday.

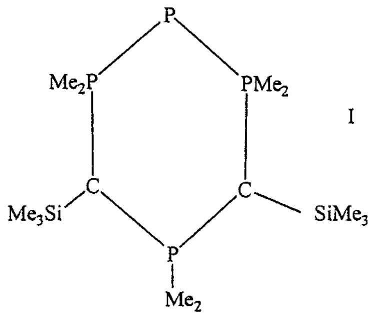
shifts and coupling constants were comparable for the ring phosphorus atoms in each case. Two different eight-membered ring neutral compounds, each containing two separate units of three linked phosphorus atoms have also been reported [5, 6]; the crystal structures of one of these, and of its 1:1 complex with $PdCl_2$, have been determined [6]. Although the shifts of the middle phosphorus atoms were at higher frequency than in the cationic complexes previously described, the coupling constants were again of similar magnitude.

More recently, Gamper and Schmidbaur prepared a six-membered cyclic triphosphenium ion and its arsenic analog, by a similar procedure to equation (1), as shown in equation (3) [7]. For E = $P_A$, $\delta^{31}P$ values of 23.0(d) for $P_B$ and −213.4(t) ppm for $P_A$, $^1J_{P_AP_B}$ 431.4 Hz, were recorded in $CD_3CN$ solution. The crystal structure was determined for $E$ = As but not for $E$ = $P_A$.



(3)

Karsch et al. subsequently synthesized a neutral eight-membered ring compound containing two separate groups of three linked phosphorus atoms and also a six-membered heterocycle with four phosphorus atoms in the ring, three of them linked, from reaction of $PCl_3$ with $LiC(PMe_2)_2(SiMe_3)$ in different solvents [8]. The crystal structure of the latter, (**I**), formed in THF, was ascertained. A similar four-membered ring was obtained by reaction of $PCl_3$ with $LiC(PPh_2)_2(SiMe_3)\cdot$TMEDA in THF, and characterized by X-ray crystallography [9]. The analog of **I** with all methyl groups replaced by phenyl was detected as a by-product from this reaction [10]. These neutral species have smaller shift differences between $P_A$ and $P_B$, and smaller $^1J_{P_AP_B}$ values (between 250 and 350Hz) than the triphosphenium cations.



I

In the present work, we show that phosphorus (III) halides $PX_3$ (X = Cl, Br, or I) will react with diphosphanes, even in the absence of an added reducing agent, to form cyclic triphosphenium ions, since the diphosphane itself will act as a reducing agent. Separation of the products is then very difficult, however, since a mixture of ionic species is formed. Five-, six-, and seven-membered rings containing three linked phosphorus atoms may be synthesized in this way and readily characterized by their $^{31}P$ NMR solution spectra (only for X = Cl in the 7-membered ring case). The six- and seven-membered ring cations have been isolated as hexachlorostannates (IV), and the crystal structure of the former has been determined as its $CH_2Cl_2$ solvate. Unfortunately the crystals of the latter were unsuitable for X-ray crystal structure determination, possibly because of solvent evaporation and consequent loss of crystallinity.

## *RESULTS AND DISCUSSION*

Preliminary experiments on $PX_3$ (X = Cl, Br, or I) and 1,2-*bis*-diphenylphosphinoethane (dppe) showed that the five-membered ring cations formed readily in $CH_2Cl_2$ solution; the shifts and coupling constants of the doublet and triplet were in good agreement with those reported by Schmidpeter et al. for the $SnCl_6^{2-}$ and $AlCl_4^-$ salts [1, 4], as indicated in Table 1. In addition, a reaction between $PBr_3$, dppe, and $SnBr_2$ gave $^{31}P$ signals at $\delta$ 64.8(d) and −229.7(t)ppm, $^1J_{PP}$ 450.1 Hz. With no Sn(II) salt

**TABLE 1** $\delta^{31}P$ and $^1J_{P_AP_B}$ for Cyclic Triphosphenium Ions

| *System* | *$\delta P_B$ (ppm)* | *$\delta P_A$ (ppm)* | *$^1J_{P_AP_B}$ (Hz)* |
|---|---|---|---|
| $PCl_3$-dppe | 64.4 | −232.4 | 451.8 |
| $PBr_3$-dppe | 64.2 | −232.1 | 451.9 |
| $PI_3$-dppe | 62.9 | −232.7 | 452.6 |
| $PBr_3$-dppe-$SnBr_2$ | 64.8 | −229.7 | 450.1 |
| $PCl_3$-dppp | 23.4 | −209.1 | 422.7 |
| $PBr_3$-dppp | 23.5 | −208.9 | 422.7 |
| $PI_3$-dppp | 23.5 | −208.9 | 422.7 |
| $PCl_3$-dppp-$SnCl_2$ | 22.9 | −209.7 | 421.6 |
| $PCl_3$-dppE | 71.9 | −248.4 | 472.9 |
| $PBr_3$-dppE | 71.8 | −247.6 | 473.0 |
| $PI_3$-dppE | 70.9 | −246.9 | 472.9 |
| $PCl_3$-dppE-$SnCl_2$ | 71.2 | −247.6 | 473.0 |
| $PBr_3$-dppE-$SnBr_2$ | 71.5 | −247.1 | 471.9 |
| $PCl_3$-dppb | 34.3 | −210.9 | 454.6 |
| $PCl_3$-dppb-$SnCl_2$ | 34.1 | −211.2 | 454.3 |

present, the other product should be either dppeX$^+$ X$^-$ or dppeX$_2^{2+}$ 2X$^-$, depending on the proportions of reagents taken, equations (4) and (5).

$$PX_3 + 2dppe \rightarrow [cation]^+ X^- + dppe\ X^+X^- \quad (4)$$

$$2PX_3 + 3dppe \rightarrow [cation]^+ X^- + dppe\ X_2^{2+}\ 2X^- \quad (5)$$

where [cation] is as shown in equations (1) and (2).

A further complication is possible for the heavier halogens in particular, since X$^-$ can then act as an acceptor for X$_2$, as in equation (6)

$$PX_3 + dppe \rightarrow [cation]^+ X_3^- \quad (6)$$

In practice a mixture of ionic products frequently resulted, with some components often precipitating out of solution. The dppe derivatives in equations (4) and (5) should in principle be distinguishable by $^{31}$P NMR spectroscopy, since dppeX$^+$ X$^-$ should give rise to two doublets from inequivalent phosphorus atoms, while dppeX$_2^{2+}$ 2X$^-$ should give a singlet. The exact shifts (and even the coupling constants in the doublets) may be affected by other factors, however, such as the extent of ionization, which in turn will depend on solvent, temperature, and other species present in solution. In the chloro-systems, single peaks between $\delta$ 66 and 30 ppm could reasonably be assigned to (partially ionized) dppe·Cl$_4$, whereas pairs of doublets between $\delta$ 42.6 and 29.1 ppm, and between $\delta$ −6.8 and −12.3 ppm respectively, $^3J_{PP}$ 51.4 ± 3.2 Hz, were ascribed to (partially ionized) dppe·Cl$_2$. The higher frequency signals correspond to the P with X attached. Similarly, broad single peaks between $\delta$ 60 and 50 ppm were often seen in bromo-systems, and probably arise from dppe·Br$_4$. These products were not investigated further because they were not the main focus of the research.

Similar reactions with *bis*-1,3-diphenylphosphinopropane (dppp) led to the formation of the analogous six-membered ring triphosphenium ions (Table 1). Clear pairs of doublets for dpppX$^+$ X$^-$ were not found in any of the systems, but single peaks, probably due to (partially) ionized dpppX$_2^{2+}$ 2X$^-$, were usually detected. In the presence of SnCl$_2$ to form the hexachlorostannate, $^{31}$P NMR data of $\delta$P$_B$ 22.9(d), $\delta$P$_A$ −209.7(t) ppm, $^1J_{P_AP_B}$ 421.6 Hz, were recorded. This salt was isolated as its CH$_2$Cl$_2$ solvate, and its crystal and molecular structure were determined (Figure 1).

Some difficulty was encountered in refining the structure because of the presence of disordered solvent (CH$_2$Cl$_2$) molecules; nevertheless the heterocyclic ring was clearly defined. Selected bond lengths and angles are given in Table 2. The P–P distances at 2.132(1) Å are marginally longer than in the five-membered ring (2.122(1) and 2.128(2) Å) [1] and are comparable with those in the neutral six-membered ring compound **I** (Structure 1) (2.134(1)Å) [8]. They are again intermediate in length between normal phosphorus-phosphorus single (2.20–2.25 Å) and double (2.00–2.05 Å) bonds [3]. The bond angle at the central phosphorus is 96.44(6)°, larger, as expected, than in the five-membered ring (88.9(1)°) [1], although slightly smaller than in compound **I** (98.1(1)°) [8]. The results are thus consistent with considerable charge delocalization over the phosphorus atoms. The C–C and C–P bond lengths are very similar to those in the five-membered heterocycle, whereas the ring bond angles at the outer phosphorus atoms and at each carbon are all comparable (113.2(1)–113.5(4)°), and larger than in the five-ring (106.5(1)–107.9(2)°) [1].

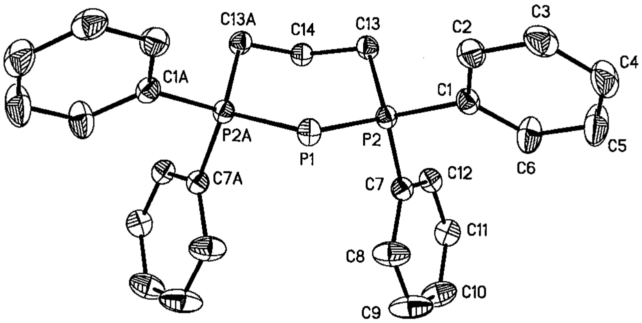


**FIGURE 1** ORTEP drawing of the cation of the title compound, showing 70% probability displacement ellipsoids for non-H atoms. H-atoms, bound to C-atoms, have been suppressed for clarity.

**TABLE 2** Selected Bond Lengths and Angles for the Cyclic Triphosphenium Cation

| *Bond Length* (*Å*) | | *Bond Angle* (*Å*) | |
|---|---|---|---|
| P(1)–P(2) | 2.132(1) | P(2)–P(1)–P(2A) | 96.44(6) |
| P(1)–P(2A) | 2.132(1) | P(1)–P(2)–C(13) | 113.2(1) |
| P(2)–C(13) | 1.815(3) | P(2)–C(13)–C(14) | 113.4(2) |
| C(13)–C(14) | 1.535(4) | C(13)–C(14)–C(13A) | 113.5(4) |
| C(14)–C(13A) | 1.535(4) | C(1)–P(2)–C(7) | 105.9(1) |
| P(2)–C(1) | 1.810(3) | C(1)–P(2)–C(13) | 110.2(1) |
| P(2)–C(7) | 1.815(3) | C(7)–P(2)–(P1) | 103.4(1) |

Analogous reactions with the unsaturated diphosphane Ph$_2$PCH = CHPPh$_2$ (dppE) again led to the formation of five-membered ring cyclic triphosphenium ions; the NMR data are collected in Table 1. Comparable results were obtained by reaction of dppE with PCl$_3$ and SnCl$_2$, and with PBr$_3$ and SnBr$_2$ (Table 1), but no crystals suitable for X-ray study were obtained from either solution. None of the $^{31}$P spectra showed the pairs of doublets expected for the unsymmetrical species dppEX$^+$X$^-$, although weak singlets in some cases probably arise from dppEX$_2^{2+}$, with varying degrees of ionization and/or differing counterions.

Diphosphane Ph$_2$P(CH$_2$)$_4$PPh$_2$ (dppb), which would lead to seven-membered ring systems, reacted slightly differently. The usual doublet and triplet were observed from reaction with PCl$_3$, Table 1. A yellow solid precipitated from the PBr$_3$ reaction, and no multiplets were detected in the solution spectra. Similar behavior was observed with PI$_3$, with rapid precipitation of a solid. Reaction of dppb with PCl$_3$ in the presence of SnCl$_2$ led to slow crystallization of pale yellow crystals, but although X-ray data were collected the structure could not be solved. It was thought that loss of solvent (CH$_2$Cl$_2$) might be occurring from the crystals. A second attempt also failed to produce crystals of X-ray quality. The solution spectra showed the expected multiplets, Table 1. There is thus no doubt that the seven-membered ring cyclic triphosphenium ion can be formed. Singlet peaks assignable to dppbCl$_2^{2+}$ with differing counterions (Cl$^-$, SnCl$_6^{2-}$ or even Cl$_3^-$) were detected in each instance, but no pairs of doublets for dppbCl$^+$.

There is no obvious correlation between $\delta$P$_A$, $\delta$P$_B$, or the coupling constant with ring size, although the unsaturated diphosphane dppE gives the largest separation between $\delta$P$_A$ and $\delta$P$_B$, as well as the largest $^1J_{P_AP_B}$ value. More work on related systems is needed before the results can be rationalized further.

In conclusion, we have shown that five-, six-, and seven-membered ring cyclic triphosphenium ions may be formed by reaction of appropriate phosphorus (III) halides and diphosphanes, even in the absence of a reducing agent such as SnCl$_2$. The crystal and molecular structure of the six-membered ring cation as its hexachlorostannate(IV)-dichloromethane solvate have confirmed the delocalized nature of the charge on the ring. If the three phosphorus atoms are regarded as shown in Figure 2, with negative charge mainly located on P$_A$, this could help to explain the high shielding of the central phosphorus atom P$_A$, as shown by its low-frequency NMR shift in all systems studied, while the two P$_B$ atoms are positively charged as quasi-phosphonium ions [6, 8, 9, 10, 11].

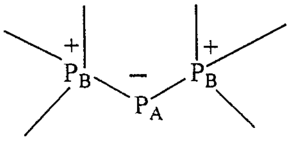


**FIGURE 2** Probable charge distribution over the phosphorus atoms in cyclic triphosphenium ion.

## EXPERIMENTAL

All manipulations were carried out either under an inert atmosphere of dry nitrogen or in vacuo, using standard Schlenk procedures or a glovebox. Chemicals of the best available commercial grade were used, in general without further purification. The $^{31}$P NMR spectra of all phosphorus-containing starting materials were checked to verify the absence of any major impurities. A solution of dppE in CH$_2$Cl$_2$ showed a very strong peak for the compound at −22.4 ppm, and two much weaker resonances at −6.5 and −11.6 ppm. These impurities were not expected to pose a problem in peak identification because of their low intensities, and the reactions were carried out as described. For PI$_3$ reactions, a standard solution of the compound in CH$_2$Cl$_2$ was prepared, and the required volume of solution to give the desired stoichiometry then calculated. The calculated volumes of PBr$_3$ or PCl$_3$ were similarly added by syringe to a solution of the appropriate diphosphane in CH$_2$Cl$_2$. For reactions involving SnX$_2$ also (X = Cl or Br), the solid materials were weighed separately, dissolved in CH$_2$Cl$_2$ in the glovebox, and the phosphorus trihalide then added by syringe.

### *Preparation of 1,1,3,3-Tetraphenyl-tetrahydro-1,2,3-triphosphenium Hexachlorostannate*

PCl$_3$ ($2.28 \times 10^{-3}$ mol) was added to a colorless solution of dppp ($2.28 \times 10^{-3}$ moles) and SnCl$_2$ ($2.28 \times 10^{-3}$ mol) in 50 cm$^3$ CH$_2$Cl$_2$, causing a color change to pale yellow; a small amount of white powder, believed to be undissolved SnCl$_2$, was filtered off using a cannula, and the remaining solution was left in the fridge. Crystals formed slowly and were separated after several weeks. The product appeared to be air-stable. C, H, and Cl analyses were consistent with the presence of some CH$_2$Cl$_2$ in the crystals (found: C, 49.3; H, 3.88; Cl, 22.9%; C$_{54}$H$_{52}$Cl$_6$P$_6$Sn requires C, 53.2; H, 4.30; Cl, 17.5%; C$_{55}$H$_{54}$Cl$_8$P$_6$Sn requires C, 50.7; H, 4.18; Cl, 21.8%; C$_{56}$H$_{56}$Cl$_{10}$P$_6$Sn requires C, 48.5; H, 4.07; Cl, 25.5%). This was confirmed by X-ray crystallography. (Lists of atomic coordinates and complete geometry have been deposited with the Cambridge Crystallographic Data Centre, CCDC 13622Y).

Single crystal structure determination of the title compound was carried out from data collected using graphite monochromated Mo K$\alpha$ radiation ($\lambda$ = 0.71073) on a Bruker SMART-CCD detector diffrac-

**TABLE 3** Crystal Data and Structure Refinement Parameters

| *Empirical Formula* | $C_{55}H_{54}Cl_8P_6Sn$ |
|---|---|
| Crystal System | Tetragonal |
| Space Group | I4/m |
| Crystal Size (mm) | 0.32 × 0.11 × 0.10 |
| $a$(Å) | 15.993(2) |
| $b$(Å) | 15.993(2) |
| $c$(Å) | 23.585(3) |
| $\alpha$(°) | 90 |
| $\beta$(°) | 90 |
| $\gamma$(°) | 90 |
| Volume(Å) | 6032.5(13) |
| Z | 4 |
| Formula Weight | 1303.22 |
| Density/g $cm^{-3}$ | 1.433 |
| $\mu$/$mm^{-1}$ | 0.972 |
| $R_{int}$ | 0.0431 |
| Observed data [$I > 2\sigma(I)$] | 3538 |
| R Indices [$I > 2\sigma(I)$] | R1 = 0.0456, wR2 = 0.1461 |
| R Indices (all data) | R1 = 0.0625, wR2 = 0.1564 |
| Goodness of Fit (S) | 1.116 |
| No. of Variables | 185 |

tometer equipped with a Cryostream N2 flow cooling device [12]. Series of narrow $\omega$-scans (0.3°) were performed at several $\phi$-settings in such a way as to cover a sphere of data to a maximum resolution of 0.70 Å. Data collection was carried out at 150(2) K. Cell parameters were determined and refined using the SMART software [13] from the centroid values of 464 reflections with $2\theta$ values between 13.6 and 21.8°. Raw frame data were integrated using the SAINT program [14]. The structure was solved using direct methods and refined by full-matrix least squares on $F^2$ using SHELXTL [15].

A yellow, rectangular prismatic crystal with dimensions 0.32 × 0.11 × 0.10 $mm^3$ was used for the measurements. A total of 37,543 reflections were measured, which merged to 4470 unique data. The tetragonal space group I4/m cannot be determined unambiguously from the systematic absences, although a clearly satisfactory refinement of the structure in I4/m confirmed this space group assignment. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms bound to carbon atoms belonging to phenyl rings were placed in geometrically calculated positions and given isotropic atomic displacement parameters 1.2 times that of the parent atom. Hydrogen atoms bound to methylene carbons were located from difference fourier maps, and their coordinates and isotropic adps were refined. Data was corrected by absorption by a semiempirical method from equivalent reflections, $T_{min}$ = 0.742, $T_{max}$ = 0.862 [16, 17]. Disordered dichloromethane is present in the structure. It has been modeled as half a molecule of $CH_2Cl_2$ occupying two different, but very close, positions. The two largest peaks in the final Fourier difference map, of around 3 e.$Å^{-3}$, are situated nearby these positions as well as several other 1 e.$Å^{-3}$ peaks. Modeling of these residual peaks has not been possible.

Crystal data and details for the structure determinations and refinements are given in Table 3. Selected bond distances and angles are given in Table 2.

$^{31}P$ NMR spectra were recorded on Varian VXR400 or Varian Mercury 200 Fourier-transform spectrometers, at 161.91 and 80.96 MHz, respectively. Chemical shifts were measured relative to external 85% $H_3PO_4$, with the higher frequency direction taken as positive. C and H microanalyses were determined by combustion on a CE-440 Elemental Analyser, and chlorine was determined by potentiometric titration against M/100 $AgNO_3$ solution using Ag/AgCl electrodes in an acetone medium, by the analytical services within the Chemistry Department.

## *ACKNOWLEDGMENTS*

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