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The Identification of Some Novel Four-Membered Ring Cyclic Triphosphenium Ions in Solution

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ABSTRACT: *The first four-membered ring cyclic triphosphenium ions with carbon substituents (methyl or cyclohexyl) on the outer phosphorus atoms have been identified in solution by ^{31}P NMR spectroscopy. The cyclohexyl derivative in the presence of $[SnCl_6]^{2-}$ as counterion was stable enough for methylation by methyl triflate to be carried out.* © 2004 Wiley Periodicals, Inc. Heteroatom Chem 15:464–467, 2004; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.20043

INTRODUCTION

Since the report of the first cyclic triphosphenium ion by Schmidpeter and co-workers in 1982 [1], several of these species with three linked phosphorus atoms in a heterocyclic ring and an overall positive charge have been described for five-, six-, or seven-membered rings [2–8]. While neutral four-membered heterocycles containing three linked phosphorus atoms and carbon substituents are known [9], however, the only cationic examples have two $-NEt_2$ or –morpholino groups on each of the outer phosphorus atoms, where the nitrogen atoms will assist in delocalization of the formal positive charge [10]. Cyclic triphosphenium ions may be readily recognized in solution by the low frequency ^{31}P NMR shift of the central bare (P_A) phosphorus atom, and the large $^1J_{PP}$ coupling constant [1–8]. Early experiments with bis-diphenylphosphinomethane (dppm) and PCl_3, with or without the presence of $SnCl_2$, yielded no NMR evidence for ring formation, although some interesting color changes to yellow and then orange were observed, even at low temperature (195 K) [11]. We have now carried out reactions between $R_2PCH_2PR_2$ (R = Me or *cyclo*hexyl) and PCl_3, in the absence or presence of $SnCl_2$, and obtained clear spectroscopic evidence for the formation of the four-membered ring cyclic triphosphenium ion in each case. While the methyl compound was fairly unstable, allowing no chemistry to be carried out, the *cyclo*hexyl derivative has been successfully methylated by methyl triflate [12] to form the corresponding dication, again unequivocally identified by ^{31}P NMR solution spectroscopy.

RESULTS AND DISCUSSION

Direct reaction between bis-dimethylphosphinomethane (dmpm) and PCl_3 in an NMR tube resulted in the precipitation of a white solid, Eqs. (1) and/or (2).

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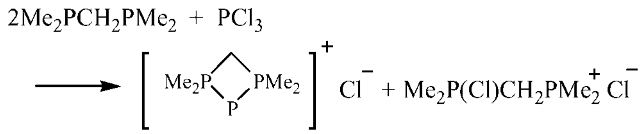

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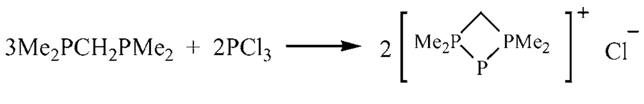
(1)



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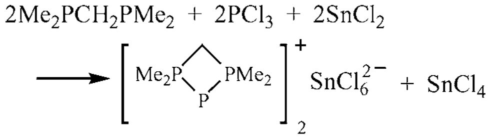
$+\ Me_2P(Cl)CH_2P(Cl)Me_2{}^{2+}2Cl^-$ (2)

Some $CDCl_3$ was added to provide a deuterium lock, and the ^{31}P NMR spectrum was recorded. A new medium-intensity doublet and triplet were observed, ($\delta\,^{31}$P 21.3 (d), −153.7(t) ppm), $^1J_{PP}$ 449 Hz) from the four-membered ring **1**, together with signals assignable to $dmpmCl^+\ Cl^-$ (two doublets, $\delta\,^{31}$P 98.2 and –48.9 ppm, $^2J_{PP}$ 70 Hz), $dmpmCl_2^{2+}\ 2Cl^-$ ($\delta\,^{31}$P 65.7(s) ppm) and dmpmO (two doublets, $\delta\,^{31}$P 33.7 and –49.3 ppm, $^2J_{PP}$ 84 Hz). The signals from the new ring had disappeared by the following morning, suggesting that it was of limited stability and/or solubility. The experiment was repeated with $SnCl_2$ also present in a 1:1:1 molar ratio, Eq. (3), but the addition of PCl_3 to the mixture of the diphosphane and $SnCl_2$caused the immediate formation of a cream precipitate. Attempts at recording solution-state NMR spectra in a variety of deuterated solvents were unsuccessful. The solid was isolated, dried, and analyzed for C and H content. The values were lower than required for **1** as its hexachlorostannate(IV) (calc. C 18.05, H 4.24%; found C 15.91, H 3.76%), suggesting the presence of some unreacted $SnCl_2$ or other tin-containing by-product (Eq. (3)), and confirming that the solid is a mixture. Mass spectrometry (EI) showed a very weak peak at 167 corresponding to the ring, and more intense peaks for possible fragments of this containing P_3 residues, supporting the contention that the ring had formed. We thus conclude that formation of the four-membered ring **1** occurs, but that its stability is limited. In consequence its chemistry could not be further investigated.



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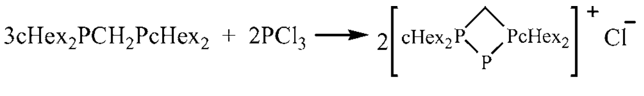
(3)

Experiments with bis-(dicyclohexylphosphino)-methane (dcxpm) were more successful. Reaction between excess PCl_3 and dcxpm, Eq. (4), resulted in the appearance of new signals at $\delta\,^{31}$P 45.1 (d) and –214.6(t) ppm, $^1J_{PP}$ 333 Hz, from **2**, and no precipitate. These signals disappeared over the course of a weekend, again suggesting that the system was of limited stability. A 1:1:1 reaction between dcxpm, $SnCl_2$, and PCl_3, Eq. (5), led to ^{31}P resonances at 45.4(d) and –216.1(t) ppm, $^1J_{PP}$ 331 Hz, confirming formation of the cation **2**. This solution remained stable for a longer period of time, enabling a methylation reaction with methyl triflate [12] to be attempted. As usual in this type of reaction [12], two equivalents of the methylating agent were required, leading to the appearance of a new doublet and triplet for the triphosphanediium ion **3**, Eq. (6), ($\delta\,^{31}$P 33.6(d), −35.1(t) ppm, $^1J_{PP}$ 195 Hz).



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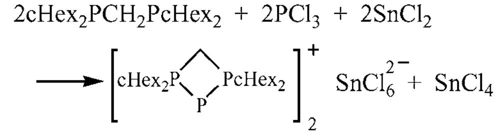
$+\ cHex_2P(Cl)CH_2P(Cl)cHex_2{}^{2+}\,2Cl^-$ (4)



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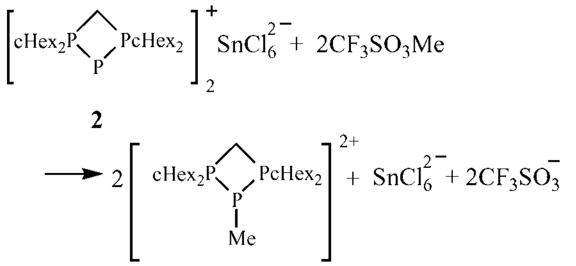

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(6)

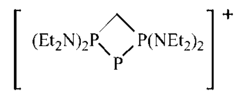
The ^{31}P NMR data for **1, 2**, and **3** are listed in Table 1, together with results for the two previously reported cationic four-membered rings with nitrogen substituents on P_B [10], and for the corresponding five-membered ring cyclic triphosphenium ions with methyl [7] or *cyclo*hexyl substituents on P_B. For the systems where comparison is possible, there is a marked shift of the P_A resonance to higher frequency on going from the five- to the four-membered ring (58.8 ppm for methyl and 75.8 ppm for *cyclo*hexyl), while the P_B signal moves to slightly lower frequency (by 38.6 and 42.4 ppm, respectively). The only mildly surprising feature of the results is that $^1J_{PP}$ for **1** is slightly higher than that for its five-membered ring analogue [7], whereas $^1J_{PP}$ for **2** is markedly lower and is comparable with the values for the species with nitrogen substituents on the outer P atoms [10].

TABLE 1 ^{31}P NMR Data

Cation	*Counterion*	*δP$_A$ (ppm)*	*δP$_B$ (ppm)*	*$^1J_{PP}$ (Hz)*	*Reference*
1	Cl^-	−153.7	21.3	449	
2	Cl^-	−214.6	45.1	333	
2	$SnCl_6^{2-}$	−216.1	45.4	331	
3	$SnCl_6^{2-}/CF_3SO_2Me^-$	−35.1	33.6	195	
4	$AlCl_4^-$	−90	56	347	[10]
5	$AlCl_4^-$	−126	56	358	[10]
6	$SnCl_6^{2-}$	−212.5	59.9	437	[7]
7	Cl^-	−290.4	87.5	458	

This difference in behavior presumably arises from variations in the electron distribution. In all cases the value of $^1J_{PP}$ is significantly reduced on methylation; $^1J_{PP}$ for **3** is ∼59% of the value for **2**. A reduction is expected for a change of hybridization, and this result is comparable with those for other cyclic triphosphenium ions [12], where $^1J_{PP}$ in the methylated species lies between 62 and 68% of the value for its unalkylated precursor. Both the shift and coupling constant changes on methylation parallel those in other systems [12], and the results provide compelling evidence for the formation of the four-membered ring **2**, and its successful methylation to **3**.

We have thus demonstrated that the synthesis of four-membered ring cyclic triphosphenium ions is feasible, and that with a suitable choice of substituent these can be sufficiently stable, particularly if soluble in the presence of a larger counterion such as $[SnCl_6]^{2-}$, to allow chemical reactions to be performed.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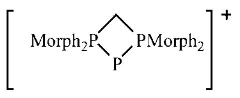
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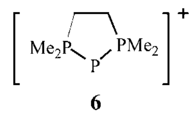
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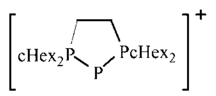
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EXPERIMENTAL

All manipulations, including NMR sample preparation, were carried out either under an inert atmosphere of dry nitrogen or in vacuo. 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 recorded before reaction, to check that no major impurities of other phosphorus compounds were present. ^{31}P NMR spectra were recorded on Varian Mercury 200, Varian Unity 300, or Varian VXR 400 Fourier-transform spectrometers, at 80.96, 121.40, and 161.91 MHz, respectively; chemical shifts were measured relative to external 85% H_3PO_4. Air-sensitive EI mass spectrometry was carried out on a Micromass Autospec mass spectrometer. The sample was run using a direct insertion probe, and the spectrum was recorded at an electron energy of 70 eV. Microanalyses were performed by the microanalytical services of the Department of Chemistry, University of Durham.

Reaction between dmpm and PCl$_3$

The ^{31}P NMR spectrum of bis(dimethylphosphino)-methane showed a single resonance at δ −53.5 ppm (lit. −55.7 ppm in C_6D_6 [13]). A small amount of the liquid diphosphane was placed in an NMR tube in a glovebox, and a few drops of PCl_3 were added, resulting in the precipitation of a white solid. Some $CDCl_3$ was added to provide a deuterium lock, and the ring signals from **1** were detected in solution (Section Results and Discussion). A quantitative reaction between $SnCl_2$ (0.2764 g, 1.46 mmol), dmpm (0.23 ml, 1.45 mmol), and PCl_3 (0.13 ml, 1.49 mmol) in CH_2Cl_2 as solvent led to an immediate cream precipitate when the PCl_3 was added to the $SnCl_2$–diphosphane mixture, and no ^{31}P NMR solution spectra could be obtained in $CDCl_3$, CD_2Cl_2, $(CD_2Cl)_2$, or $C_6D_5NO_2$. The solid was separated by filtration and dried in vacuo. Characterization was attempted via elemental analysis and mass spectrometry (Section Results and Discussion); as expected, however, the product was clearly a mixture, although some evidence was found for formation of the ring from the mass spectrum.

Reaction between dcxpm and PCl$_3$

The ^{31}P NMR spectrum of dcxpm showed a single peak at δ −8.9 ppm; some minor impurity peaks were also visible. 0.0140 g (0.030 mmol) dcxpm was weighed into a Young's NMR tube, and 0.5 ml of CH_2Cl_2 was added. 0.01 ml (0.11 mmol) PCl_3 was added by syringe, followed by 0.5 ml of $CDCl_3$. The signals for the ring **2** were detected when the ^{31}P NMR spectrum was recorded ca. 30 min later. These signals disappeared when the solution was left over the weekend, suggesting that the stability of the ring was limited. The reaction was therefore repeated with $SnCl_2$ present also. 0.0542 g (0.13 mmol) dcxpm was dissolved in 0.5 ml CH_2Cl_2 in a Young's NMR tube, and 0.5 ml $CDCl_3$ was added. 0.0246 g (0.13 mmol) $SnCl_2$ was dissolved in 0.05 ml CH_2Cl_2, and the solution added to the NMR tube. Finally 0.01 ml (0.11 mmol) PCl_3 was syringed in to the tube. The doublet and triplet for the new ring **2** (Section Results and Discussion) were clearly apparent when the ^{31}P NMR spectrum was recorded ca. 30 min after mixing.

Reaction between Cation 2 and Methyl Triflate

A new solution of the ring was prepared as above from 0.0370 g (0.09 mmol) dcxpm, 0.0172 g (0.09 mmol) $SnCl_2$, and 0.01 ml (0.11 mmol) PCl_3. Formation of the ring was confirmed by recording its ^{31}P NMR spectrum after ca. 30 min (δ P_A – 215.1, δ P_B 46.2 ppm, $^1J_{PP}$ 331 Hz). 0.01 ml (0.09 mmol) methyl triflate was added, but there was no immediate change in the spectrum. The next day a second equivalent quantity of methyl triflate was added, and a new doublet and triplet corresponding to the methylated ring **3** as well as the signals from **2** were apparent in the ^{31}P NMR spectrum recorded after ca. 2 h. Crystals formed in the NMR tube after 3 d, but attempted single crystal X-ray diffraction showed that these were twinned, and no structure could be obtained.

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