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Methylation of Some Cyclic Triphosphenium Ions

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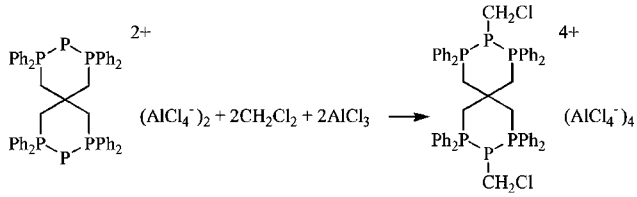
ABSTRACT: *Six cyclic triphosphenium ions, including examples of five-, six-, and seven-membered ring systems, have been successfully methylated by excess methyl triflate to form the corresponding dications. This has been unequivocally established by means of ^{31}P NMR spectroscopy; results are in good agreement with literature data for this type of compound.* © 2004 Wiley Periodicals, Inc. Heteroatom Chem 15:150–154, 2004; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.10228

INTRODUCTION

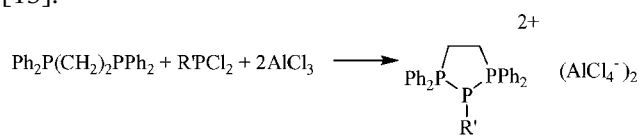
The first cyclic triphosphenium ion **1** (Scheme 1) was described and fully characterized, including a single crystal X-ray molecular structure as its hexachlorostannate(IV) salt, by Schmidpeter and coworkers in 1982 [1]. Subsequently several other examples have been reported, including ions with a five-membered ring [1–6], a six-membered ring [4–7], two linked six-membered rings [4,7], and a seven-membered ring [5,6], as well as four- [8] and eight-membered neutral species with either one [9,10] or two [11,12] units of three linked phosphorus atoms. The ions are all characterized by a low-frequency ^{31}P NMR shift for the central phosphorus atom and a large $^{1}J_{PP}$ (>400 Hz) value. Where molecular structures have been ascertained, the P–P distances are intermediate between normal single and double P–P bonds [1,5,6]. The chemistry of cyclic triphosphenium ions has been comparatively little investigated, however. Schmidpeter et al. demonstrated that protonation of the central phosphorus atom in **1** was possible by using $AlCl_3$ and $^{t}BuCl$ [4,13]; we have more recently extended this work to a number of other cyclic systems [Burton, J. D.; Deng, R. M. K.; Dillon, K. B.; Olivey, R. J. in preparation]. The only report of a successful alkylation is for the dication **2** derived from tetraphos, which was chloromethylated by a mixture of CH_2Cl_2 (2 mol) and $AlCl_3$ (2 mol) to form a tetracationic species **3**, Eq. (1) [4].



2 **3**

(1)

Compound **3** gave rise to an $[A_2B]_2$ $^{31}P\{^{1}H\}$ NMR spectrum, with δ P_A 8.7, δ P_B −79.8 ppm, $^{1}J_{PP}$ 282.4 Hz, compared with δ P_A 17.6, δ P_B −249.6 ppm, $^{1}J_{PP}$ 440.5 Hz for **2**. As expected, the central phosphorus atom P_B showed a far larger shift change on alkylation than the outer phosphorus atoms P_A, and the P–P coupling constant was substantially reduced. Two similar dicationic derivatives **4** and **5** of single-ring cyclic triphosphenium ions have been synthesized from noncyclic precursors, according to Eq. (2) [13].



4 R' = CH_2Cl
5 R' = ^{t}Bu

(2)

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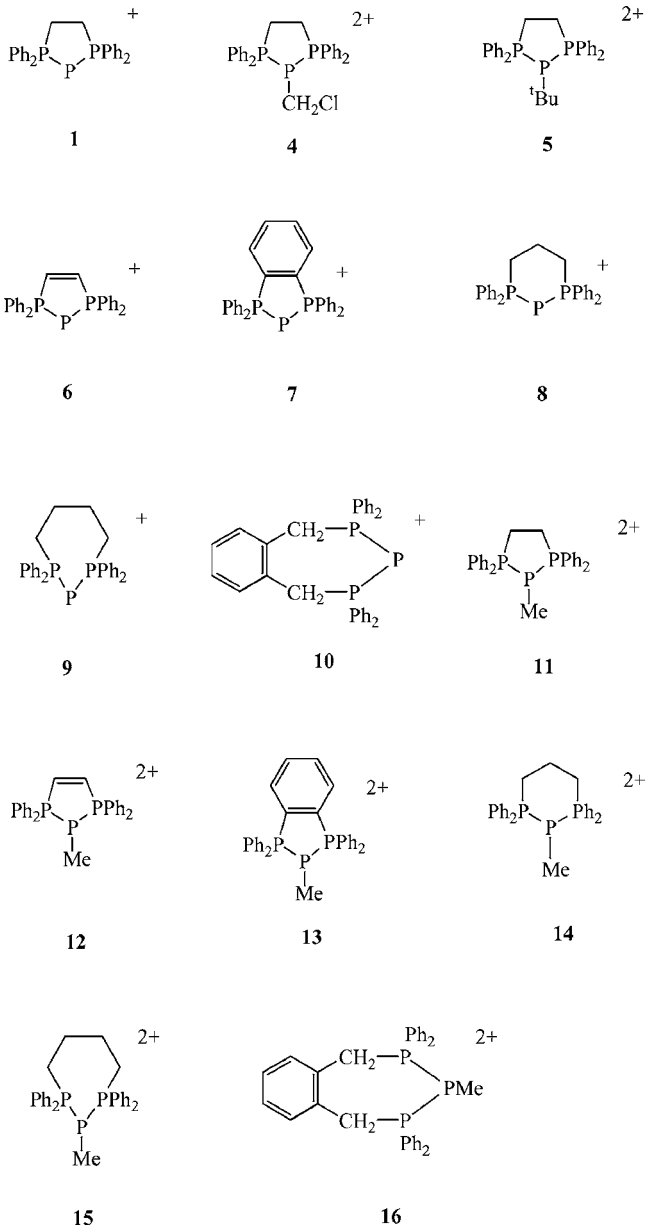


SCHEME 1

The NMR data for **4** (δ P_A 52, δ P_B −78 ppm, $^1J_{PP}$ 282 Hz) and **5** (δ P_A 52, δ P_B −79 ppm, $^1J_{PP}$ 283 Hz) were very similar to those for **3**. In view of the existence of these species, there seemed no good reason why direct alkylation of cyclic triphosphenium ions should not be possible. In this work we report on the successful methylation of a number of cyclic triphosphenium ions, using methyl triflate as the alkylating agent; an excess of the latter reagent was usually required. A preliminary experiment involving an attempted stoichiometric (1:1) reaction between cyclic triphosphenium ion **1** and iodomethane was unsuccessful, however, providing no evidence for alkylation [14; Dillon, K. B.; Wilkinson, J. J. unpublished work].

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 the diphosphanes were recorded before reaction, to verify that no major phosphorus-containing impurities were present. Some small impurity peaks were found in the spectrum of α,α′-bis(diphenylphosphino)-*o*-xylene, the precursor of **10**, but these did not affect the assignment of the main resonances. ^{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. The ring systems **1** and **6–10** were prepared from 2:3 reactions between PCl_3 and the diphosphane in dichloromethane as solvent, Eq. (4), as described previously [5,6]. The mixtures were allowed to stir at room temperature to complete the reaction as far as possible. After confirming that the cyclic triphosphenium ion had formed, an equimolar quantity of methyl triflate to that of the PCl_3 used was added by syringe. Often further aliquots of methyl triflate were required (Section Results and Discussion) to complete the methylation.

RESULTS AND DISCUSSION

As mentioned above, a stoichiometric (1:1) reaction between cyclic triphosphenium ion **1** (as its chloride salt) and MeI provided no evidence for methylation of the ring, the only cyclic species detected being the starting material **1** [14; Dillon, K. B.; Wilkinson, J. J. unpublished work]. Since the ring appeared to survive these conditions, the more powerful methylating agent methyl triflate was utilized in the present work. Six representative cyclic triphosphenium ions **1** and **6–10** (Scheme 1) were generated in situ from PCl_3 and the appropriate diphosphane, as described in earlier papers [5,6]. As can be seen from Scheme 1, these include examples of five-, six-, and seven-membered ring species. The results will be described

for each system individually. In each case the ^{31}P NMR spectrum of the solution was recorded to check that the cyclic triphosphenium ion had formed, before addition of methyl triflate.

When an equimolar quantity of methyl triflate was added to **1** (as its chloride), no methylation of the ring was observed in the NMR spectrum immediately, or after 1 day. A second equimolar amount was added, and a new weak doublet and triplet were detected, ascribed to the methylated dication **11**, although the original ring was still present after a further 3 days. Two more equivalents of methyl triflate (all volumes of methyl triflate were measured quantitatively, by syringe) were added, and the intensity of the new doublet and triplet increased (Table 1), although a weak doublet from the original ring was still apparent. Interestingly, a weak signal at 193.2 ppm suggested that even some $MePCl_2$ had formed [15]. After another 1 day, an off-white precipitate was observed, and following separation of the solid the new ring signals had disappeared from the ^{31}P NMR spectrum of the filtrate. Elemental analysis and solid-state ^{31}P NMR of the solid showed that it was a mixture of decomposition products, however, so the stability of the methylated ring appeared to be limited under these conditions. Some small crystals were isolated from the filtrate, but these were proved by single-crystal X-ray diffraction to be $dppeH_2^{2+}(CF_3SO_3^-)_2$. A doublet signal at δ ^{31}P 11.6 ppm, $^1J_{PH}$ 533 Hz, was observed in the proton-coupled spectrum of the solution, and probably arises from this cation, either formed by protonation of some unreacted diphosphane (although none was detected), or by break-up of the ring, such as in Eq. (3). A full report of this and related crystal and molecular structures of some protonated diphosphane salts will be published elsewhere [Batsanov, A. S.; Boon, J. A.; Dillon, K. B.; Howard, J. A. K.; Olivey, R. J.; Roden, M. D. in preparation].

$$\mathbf{11} + 2\,HCl \rightarrow dppeH_2^{2+} + MePCl_2 \qquad (3)$$

The results for **11** are in very good agreement with those for **3, 4**, and **5**, as shown in Table 1, which lists the ^{31}P NMR data for all the cyclic triphosphenium ions and their alkylated dicationic derivatives. (Dications **4** and **5** were not prepared directly from the cyclic precursor, as indicated in the Section Introduction [13]; nevertheless they may properly be regarded as alkylated derivatives of **1**.) The signal from the central phosphorus atom P_B moves to much higher frequency on alkylation, and $^1J_{PP}$ is considerably reduced. The outer phosphorus atoms P_A show a small shift to lower frequency, reflecting the change in electron distribution.

The *cis*-1,2-bis(diphenylphosphino)ethene (dppE) derivative **6** was slow to form, the reaction not having gone to completion even after 4 weeks, at which point methylation was attempted. Addition of a stoichiometric (1:1) amount of methyl triflate and stirring overnight led to a small amount of precipitate, with the ring **6** still present in solution, although a new doublet assigned to the methylated product **12** was detected. Rather surprisingly, doublet and triplet signals from the norbornane-like trication **17** obtained as a by-product of protonation of the dppE ring were also observed (δ ^{31}P 54.5 t, 30.7 d ppm, $^2J_{PP}$ 27.5 Hz) [Deng, R. M. K.; Dillon, K. B.; Goeta, A. E.; Thompson, A. L. in preparation]. A second equivalent of methyl triflate was added, and the doublet and triplet from **12** were apparent (Table 1). The signals were quite weak, however, and several impurity peaks were present, suggesting that this system, too, is of limited stability and/or solubility. Signals for **17** had also disappeared by this stage.

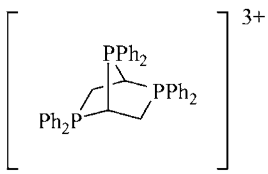
The third five-membered ring system **7** examined, with an aromatic backbone, also formed slowly, reaction being complete after ca 4 weeks. No change was seen on addition of 1 equivalent of methyl triflate, but four more equal volume additions drove the reaction to completion, with formation of the methylated product **13**, and none of the original ring **7** still present. The solution was left in the freezer to see if crystals would grow, but unfortunately this did not occur. As well as the similarity in shifts and coupling constants to those of other alkylated species (Table 1), the NMR data for the shift of the middle P_B and coupling constant $^1J_{PP}$ correspond well with those for the neutral species **18** [16] (R = Ph, δ P_B −31.5, $^1J_{PP}$ 254.1 Hz (C_6H_6) [16]; R = Ph, δ P_B −39.4, $^1J_{PP}$ 265 Hz ($CHCl_3$) [17]; R = Me, δ P_B −67.5, $^1J_{PP}$

TABLE 1 δ ^{31}P (ppm) and $^1J_{PP}$ (Hz) for Some Cyclic Triphosphenium Ions and Their Alkylated Derivatives[a]

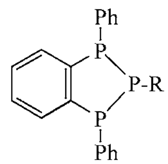
Triphosphenium Ions					*Triphosphanediium Ions*				
	δP_A	δP_B	$^1J_{PP}$	*Ref*		δP_A	δP_B	$^1J_{PP}$	*Ref*
2	17.6	−249.6	440.5	[4]	**3**	8.7	−79.8	282.4	[4]
1	65.3	−230.5	450	[5]	**4**	52	−78	282	[13]
1	65.3	−230.5	450	[5]	**5**	52	−79	283	[13]
1	65.3	−230.5	450	[5]	**11**	54.8	−91.3	284	
6	72.2	−249.1	472	[5]	**12**	57.7	−96.5	311	
7	57.6	−212.7	451	[6]	**13**	45.4	−68.6	291	
8	23.1	−209.9	424	[5]	**14**	12.5	−89.4	262	
9	34.1	−211.3	455	[5]	**15**	31.0	−75.6	308	
10	25.0	−216.0	439	[6]	**16**	15.8	−73.4	296	

[a]The data for **1** and **6–16** are those recorded in the present work.

252 Hz [18]; R = Me, δ P_B −68.8 ppm, ${}^1J_{PP}$ 251.8 Hz (THF) [16]; R = Et, δ P_B not recorded, ${}^1J_{PP}$ 255 Hz [18]).



17



18 (R = Ph, Me, or Et)

The six-membered ring 1,3-bis(diphenylphosphino)propane (dppp) derivative **8** had formed completely after 1 day. Addition of an equivalent quantity of methyl triflate and stirring overnight produced a clear solution, the ^{31}P NMR of which showed a new doublet and triplet (Table 1) from the methyl derivative **14**, as well as those from the original ring. The new triplet also showed evidence of quartet splitting of each component (${}^2J_{PH}$ 7.7 Hz) when recorded proton-coupled, arising from coupling to the methyl protons.

Similarly the 7-membered ring 1,4-bis(diphenylphosphino)butane (dppb) derivative **9** was fully formed after 3 days, with no unreacted diphosphane present. After addition of one equivalent of methyl triflate, a new doublet and triplet assigned to the methylated product **15** were apparent, although lower in intensity than the signals from **9**. Three further equimolar portions of methyl triflate were required before these signals disappeared completely. Attempts at growing crystals were again unsuccessful. Several impurity and/or decomposition product signals were now evident in the NMR spectrum, however, as well as the resonances from **15**, suggesting that **15** was not very stable in solution. These included protonated species at δ 11.7 (${}^1J_{PH}$ 510), 10.9 (${}^1J_{PH}$ 515), and 10.1 (${}^1J_{PH}$ 505 Hz) ppm, possibly from the protonation of dppb [19,20].

Seven-membered ring system **10** was also prepared; its formation was complete after 1 day. The initial addition of an equimolar amount of methyl triflate followed by overnight stirring caused the appearance of a new doublet from **16**, though two further equivalents were required before the resonances from **10** disappeared and the triplet as well as the doublet from **16** could be observed. Again there were several impurities and/or decomposition product peaks present, including two from species with P–H bonds (δ ^{31}P 9.2 ppm, ${}^1J_{PH}$ 522 Hz and δ ^{31}P 8.1 ppm, ${}^1J_{PH}$ 509 Hz), thought to arise from the protonated diphosphane or its derivatives, and suggesting that the methylated seven-membered ring is not very stable under these conditions. As mentioned in the Section Experimental, there were also small amounts of some phosphorus-containing impurities in the starting material for this system.

In all of the mixtures except the one derived from dppE (**6, 12**), signals observed late in the reaction sequence between 193.3 and 193.0 ppm suggested the formation of some $MePCl_2$ [15]. It should be pointed out that in all systems there was some PCl_3 still present even after disappearance of the resonance from the diphosphane starting material. This arises because, although the reactions were carried out stoichiometrically in a 2:3 ratio, as exemplified for dppe in Eq. (4) [5,6], this process is not a "clean" one; a 1:2 reaction is also possible, Eq. (5). It is not possible to prevent this reaction, which consumes less PCl_3 per mole of diphosphane, from occurring spontaneously with that shown in Eq. (4).

$$2PCl_3 + 3Ph_2P(CH_2)_2PPh_2 \rightarrow 2Ph_2P\overset{}{\underset{P}{}}PPh_2{}^+Cl^- + [Ph_2P(Cl)(CH_2)_2P(Cl)Ph_2]^{2+}(Cl^-)_2 \quad (4)$$

$$PCl_3 + 2Ph_2P(CH_2)_2PPh_2 \rightarrow Ph_2P\overset{}{\underset{P}{}}PPh_2{}^+Cl^- + [Ph_2P(CH_2)_2P(Cl)Ph_2]^+Cl^- \quad (5)$$

The results overall present clear evidence that methylation of five-, six-, and seven-membered ring cyclic triphosphenium ions by methyl triflate takes place as shown by Table 1. The probable reasons why excess of the reagent is required is that other species present even at low concentration in the original solution may be methylated preferentially, and that there may be a kinetic barrier to methylation of the cyclic cations. This could arise for both electronic reasons (repulsion between positive charges), and from steric hindrance by the bulky phenyl groups to the approach of the methylating agent. In this context it is interesting to note that an attempt to react **1** with ethyl triflate was unsuccessful, the original ring still being present even after the addition of four equivalents of ethyl triflate. It is also probable that the kinetic barrier to methylation will vary with ring size, with larger rings being methylated more readily. Some support for this hypothesis is provided by the observation that ^{31}P NMR signals from the methylated product were not detected for two of the three five-membered ring systems after addition of an equimolar quantity of methyl triflate, whereas some methylation was apparent under similar conditions for all of the larger rings. Further work is necessary to elucidate this point fully.

As mentioned earlier, all the NMR data are in very good agreement with results for the known

species **3–5**, included in Table 1 [4,13], and (for δ P_B and $^1J_{PP}$) with those for the neutral compounds **18** [16–18]. We therefore conclude that methylation of cyclic triphosphenium ions **1** and **6–10** is possible to form cyclic dications, although excess methyl triflate is usually required to accomplish this. The stability of the product appears to vary with the system, however.

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