Alkyl and aryl dicationic derivatives of cyclic triphosphenium ions†‡

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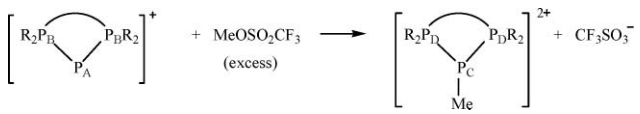
Direct alkylation of cyclic triphosphenium ions by triflates to give di-ium dications is only possible for small organic substituents on the attacking reagent. The dicationic products are not intrinsically unstable, however, and in many instances they may be synthesised by an alternative route, pioneered by Schmidpeter and co-workers. These species may be readily identified in solution by ^{31}P NMR spectroscopy. The crystal and molecular structures of five such derivatives have been ascertained for the first time by single crystal X-ray diffraction at 120 K. The results confirm that normal single P–P bond lengths are present in the dications, in contrast with the monocationic parent cyclic triphosphenium ions, where structural determinations have shown that the P–P bond lengths are intermediate between single and double bonds.

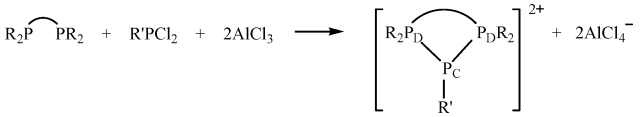
Introduction

Cyclic triphosphenium ions, containing three linked phosphorus atoms and a carbon backbone, were first prepared by Schmidpeter *et al.* over twenty-five years ago.[1] These interesting species have a 'bare' central P atom in the formal oxidation state of +1, and may be readily identified in solution by ^{31}P NMR spectroscopy. Work in this area has been well-described in a recent review.[2] In structures that have been determined by X-ray diffraction, the bond lengths are intermediate between normal P–P single and double bonds,[1–9] providing evidence for a delocalised system. The presence of the 'bare' P in a low oxidation state should facilitate oxidation reactions at this centre, and we have shown that direct methylation using excess methyl triflate is possible for many of these ions to form di-ium dications, as depicted in Scheme 1.[10,11]



Scheme 1 Direct methylation of cyclic triphosphenium ions.

Attempts to extend this approach to larger organic substituents on the attacking reagent have had only limited success, as described below. We have carried out a few direct ethylations using excess ethyl triflate, but only for small substituents on the two four-coordinate P atoms, suggesting considerable steric hindrance to the incoming reagent. This conclusion is supported by the successful synthesis of several alkyl- and aryl-substituted cyclic triphosphenium ions by an alternative route, again pioneered by Schmidpeter and co-workers, who described the preparation of two such compounds according to Scheme 2.[12]



Scheme 2 Indirect method of forming alkyl or aryl derivatives of cyclic triphosphenium ions.[12]

To date no crystal or molecular structures of these dications have been reported. In the present work, we show that a large range of derivatives may be prepared *via* this alternative route, indicating that the species are not intrinsically unstable. In all examples, the ^{31}P NMR solution-state parameters show a marked reduction in $^{1}J_{PP}$ compared with the values for the triphosphenium ions themselves. Five of these species have been isolated as salts, and further characterised by single-crystal X-ray diffraction at low temperature. In each instance the P–P distances are as expected for single bonds, confirming that the central P is now in the +3 oxidation state, and that the delocalised double bond character has been removed.

Results and discussion

A standardised numbering and lettering scheme has been adopted for the cyclic triphosphenium ions and their derivatives described in the present work. The parent diphosphanes are numbered from **1–12** as shown in Scheme 3. The cyclic triphosphenium ion corresponding to this diphosphane is taken as **a**, its P-methyl derivative as **b**, P-ethyl as **c**, P-*n*-propyl as **d**, P-isopropyl as **e**, P-*tert*-butyl as **f**, P-cyclohexyl as **g** and the P-phenyl derivative as **h**.

(a) Direct alkylation

As described previously by us,[10,11] direct methylation of several cyclic triphosphenium ions by excess methyl triflate has proved possible for ring sizes from 4–7 where the rings are sufficiently

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† Dedicated to Professor Ken Wade, FRS, on the occasion of his 75th birthday.

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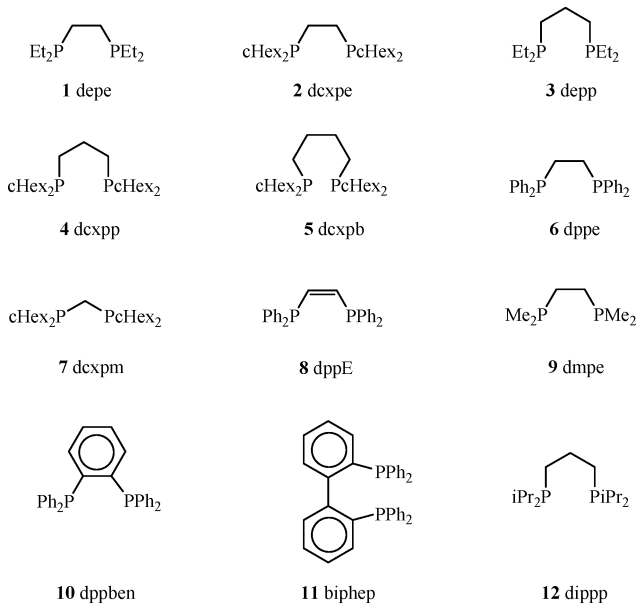


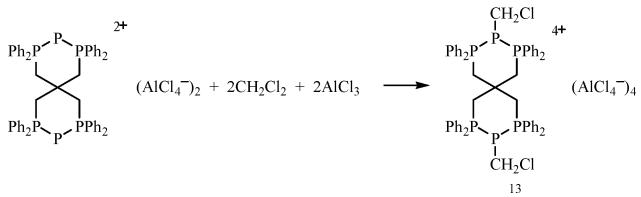
Scheme 3 Structures of the diphosphanes.

stable (Scheme 1). Some new ^{31}P NMR results are shown in Table 1, with the shifts and coupling constants of the precursor triphosphenium ions included for comparison.

In all cases the most notable features are a large higher frequency shift for the central P atom, and a marked reduction in $^{1}J_{PP}$, on methylation. The four-coordinate P atoms display a much smaller shift to lower frequency in the alkyl derivatives.

Previous attempts at direct ethylation by excess ethyl triflate had been unsuccessful,[10] but this has now been achieved for the five-membered ring cyclic triphosphenium ion derived from depe, and the six-membered ring derived from depp. The results are given in Table 2, and confirm the same trends in ^{31}P NMR data as described above for methylation. However, no direct ethylations could be achieved for cyclic triphosphenium ions with cyclohexyl, phenyl, isopropyl or *tert*-butyl substituents on the outer phosphorus atoms, strongly suggesting considerable steric hindrance to the formation of the ethyl derivatives. Ethylation is expected to occur for the ion derived from dmpe, but the reaction products proved to be too insoluble for a solution-state spectrum to be obtained. Similarly, reaction of excess phenyl triflate with the depe derivative did not lead to formation of the phenyl-substituted dication, the solution-state spectrum showing only the precursor ion, even though the dication may be readily prepared by the alternative route described below. A similar experiment on the seven-membered ring cyclic triphosphenium ion derived from 1,4-bis(diisopropyl)-phosphinobutane (dippb), in an attempt to see whether a larger ring size would aid arylation, also failed to produce the phenyl derivative.

The only report of direct alkylation before the studies mentioned above was by Lochschmidt and Schmidpeter, who successfully chloromethylated a dication to form a tetracation using a CH_2Cl_2–$AlCl_3$ mixture as the attacking reagent (Scheme 4).[13] The combined results indicate that direct alkylation is feasible for small organic substituents on the attacking reagent, particularly Me, although as pointed out previously, a large excess of methyl triflate is often required, particularly if there are any other phosphorus species in solution which would be more readily alkylated than the triphosphenium ion.[10,11]



Scheme 4 Direct chloromethylation reaction.[13]

(b) Indirect alkylation or arylation

Indirect alkylation or arylation involves the treatment of a diphosphane $R_2P(CH_2)_nPR_2$ with a dichlorophosphane $R'PCl_2$ (1 : 1) in the presence of two moles of $AlCl_3$, as shown in Scheme 2.[12] We have prepared the complete series of such derivatives in solution for R′ = Et, *n*-Pr, i-Pr, *t*-Bu, c-Hex or Ph with the diphosphanes depe (**1**) and dppe (**6**); the ^{31}P NMR data are listed in Tables 3 and 4 respectively.

Two sets of resonances were observed for the cyclohexyl derivative of the ring formed from dppe, ascribed to a mixture of Cl^- and $AlCl_4^-$ counter-ions. Their identities were established by adding more $AlCl_3$ to the mixture, which caused an increase in relative intensity for the signals at 48.9 and −75.7 ppm, so these may be assigned to the bis-$AlCl_4^-$ salt.

Table 1 ^{31}P NMR data (δ in ppm; $^{1}J_{PP}$ in Hz) for some cyclic triphosphenium ions and their P-methyl derivatives

Compound	Ion	Ring size	δP_B	δP_A	$^{1}J_{PP}$	Ion	δP_D	δP_C	$^{1}J_{PP}$
1	**1a**	5	81.7	−269.2	441	**1b**	65.7	−98.0	289
2	**2a**	5	87.3	−289.3	457	**2b**	65.1	−96.1	301
3	**3a**	6	33.4	−251.3	415	**3b**	28.1	−102.1	274
4	**4a**	6	36.2	−293.0	458	**4b**	27.0	−109.5	281
5	**5a**	7	48.1	−261.4	475	**5b**	43.4	−76.3	321

Table 2 ^{31}P NMR data (δ in ppm; $^{1}J_{PP}$ in Hz) for some cyclic triphosphenium ions and their P-ethyl derivatives

Compound	Ion	Ring size	δP_B	δP_A	$^{1}J_{PP}$	Ion	δP_D	δP_C	$^{1}J_{PP}$
1	**1a**	5	81.7	−269.2	441	**1c**	66.1	−89.8	291
3	**3a**	6	30.0	−251.3	418	**3c**	28.6	−89.8	283

Table 3 ^{31}P NMR data (δ in ppm; $^{1}J_{PP}$ in Hz) for some alkyl and aryl derivatives of depe, **1**

Substituent	Code	δP_D	δP_C	$^{1}J_{PP}$
Et	**1c**	66.0	−92.7	293
n-Pr	**1d**	62.2	−95.1	295
i-Pr	**1e**	67.3	−66.6	311
t-Bu	**1f**	66.8	−33.6	338
c-Hex	**1g**	67.0	−71.9	309
Ph	**1h**	60.2	−94.2	280

Table 4 ^{31}P NMR data (δ in ppm; $^{1}J_{PP}$ in Hz) for some alkyl and aryl derivatives of dppe, **6**

Substituent	Code	δP_D	δP_C	$^{1}J_{PP}$
Et	**6c**	53.4	−93.0	287
n-Pr	**6d**	53.8	−95.1	288
i-Pr	**6e**	49.0	−71.3	304
t-Bu	**6f**	49.5	−54.0	332
c-Hex	**6g**	50.4	−79.1	311
		48.9	−75.7	308
Ph	**6h**	53.1	−76.9	280

For all ions in both series there is a marked reduction in $^{1}J_{PP}$ compared with the triphosphenium ions **1a** (Table 1) or **6a**[1] respectively, and a large shift to higher frequency of the central phosphorus atom. The four-coordinate P atoms give a much smaller shift to lower frequency on alkylation. In these two series, $^{1}J_{PP}$ values are very similar for R′ = Et or *n*-Pr, though there is then a significant increase on going from *n*-Pr to i-Pr to *t*-Bu substituents.

Our results for the *t*-butyl derivative of the dppe system differ from those of Schmidpeter *et al.*, who reported δP_D 52, δP_C −79 ppm, $^{1}J_{PP}$ 283 Hz.[12] The present data are much more consistent with the results for the depe series, and it seems probable that under their experimental conditions they obtained the chloromethyl derivative (δP_D 52, δP_C −78 ppm, $^{1}J_{PP}$ 282 Hz) described in the same paper,[12] with this species being formed in preference to the *t*-Bu analogue.

The ethyl derivatives of a number of other cyclic triphosphenium ions have also been synthesised in solution; the ^{31}P NMR results are presented in Table 5, for various ring sizes as indicated. Table 6 gives parallel results for some other dihalophosphanes. Particularly noteworthy are the results for the four-membered ring dcxpm system with ethyl (**7c**, Table 5) or isopropyl (**7e**, Table 6) substituents. The reaction with i-PrPCl$_2$ was performed in the presence of both AlCl$_3$ and SnCl$_2$ separately; very similar results were obtained, as shown in Table 6. The NMR parameters

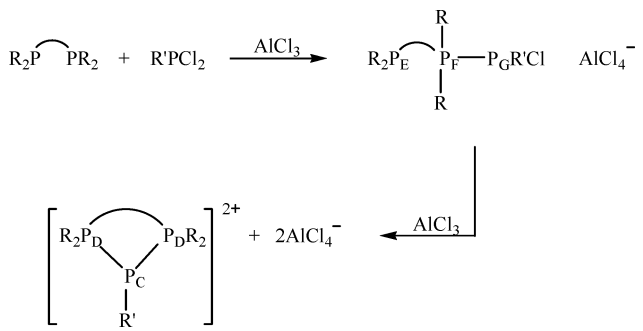
Table 5 ^{31}P NMR data (δ in ppm; $^{1}J_{PP}$ in Hz) for other ethyl derivatives of cyclic triphosphenium ions

Diphosphane	Code	Compound	Ring size	δP_D	δP_C	$^{1}J_{PP}$
dcxpm	**7**	**7c**	4	40.4	−59.7	156
dcxpe[a]	**2**	**2c**	5	57.0	−85.2	319
dppE	**8**	**8c**	5	58.9	−93.2	307
dmpe	**9**	**9c**	5	46.6	−76.4	290
dppben	**10**	**10c**	5	44.8	−66.7	286
dppben[a]	**10**	**10c**	5	45.1	−72.2	300
depp	**3**	**3c**	6	28.9	−85.8	301
dcxpp	**4**	**4c**	6	28.7	−92.4	303
dcxpb[a]	**5**	**5c**	7	32.1	−52.6	305
biphep	**11**	**11c**	7	12.8	−14.2	322

[a] $SnCl_2$ added instead of $AlCl_3$.

may be compared with those previously reported by us for the methyl (**7b**) derivative, prepared by direct methylation of the cyclic triphosphenium ion **7a**.[11] These ions have the smallest $^{1}J_{PP}$ values yet measured in such systems, parallel with data for **7a** itself, which has the smallest $^{1}J_{PP}$ value for such a species. Thus the changes caused by alkylation are not out of line with the results for larger-ring systems. The results for **6b** and **8b** are very similar to those obtained previously for these ions by direct methylation,[10] particularly when the difference in counter-ion is taken into account.

The mechanism of this indirect alkylation (or arylation) reaction necessarily involves the addition of the chlorophosphane to one of the P atoms of the diphosphane to form a P–P bond, as shown in Scheme 5. This is expected to displace a halogen, accepted by AlCl$_3$ to form a tetrachloroaluminate, as shown. Cyclisation with loss of the second halogen (in the presence of AlCl$_3$) to yield the dicationic product then follows, Scheme 5. It should be noted that the acyclic cationic intermediate is identical to that postulated in the first



Scheme 5 Mechanism of indirect alkylation or arylation reactions.

Table 6 ^{31}P NMR data (δ in ppm; $^{1}J_{PP}$ in Hz) for other alkyl or aryl derivatives of cyclic triphosphenium ions

Diphosphane	Code	R′	Code	Ring size	δP_D	δP_C	$^{1}J_{PP}$
dcxpm[a]	**7**	i-Pr	**7e**	4	38.8	−29.1	152
dcxpm[b]	**7**	i-Pr	**7e**	4	38.8	−28.9	150
dppe	**6**	Me	**6b**	5	53.2	−96.9	279
dppE	**8**	Me	**8b**	5	59.8	−97.0	301
depp	**3**	*n*-Pr	**3d**	6	30.0	−89.1	306
depp	**3**	Ph	**3h**	6	27.8	−83.7	295
dippp	**12**	*n*-Pr	**12d**	6	37.2	−92.8	288

[a] $AlCl_3$ added. [b] $SnCl_2$ added.

Table 7 ^{31}P NMR data (δ in ppm; $^{1}J_{PP}$ in Hz) for intermediates in attempted indirect alkylations

Diphosphane	Code	R′	δP_E	δP_F	δP_G	$^{1}J_{PP}$
depp	**3**	Et	17.4	57.2	−48.1	278
depp	**3**	i-Pr	18.2	57.3	−48.3	278
depp	**3**	*t*-Bu	17.5	57.2	−48.2	279
dcxpp	**4**	*n*-Pr	11.7	50.4	−28.8	309
dippp	**12**	*t*-Bu	33.3	60.1	−26.4	309

stage of formation of the novel cyclic tetraphosphonium dications, described very recently by us.[14] In the present case, however, no redox step is involved, although the reaction will undoubtedly be facilitated by the presence of a good halide acceptor. Indeed, as we have demonstrated in a previous paper,[14] a mixture of the triphosphane-di-ium dication and tetraphosphonium dication (4P) is often obtained when a diphosphane is treated with $R'PCl_2$ in the presence of $SnCl_2$. In some slowly-reacting systems, NMR spectroscopic evidence for the acyclic intermediate was found. This species is expected to give rise to two doublets with a large $^{1}J_{PP}$ for P_F and P_G (Scheme 5), and either a singlet for P_E, or a doublet with a much smaller coupling constant from P_F coupling. In this case P_F should also show fine structure (as a doublet of doublets). Weak signals were detected for depp reacting with $EtPCl_2$ (Table 7) in the process of forming **3c**, which could be assigned to P_E, P_F and P_G (Scheme 5), in the acyclic intermediate. Interestingly, ^{31}P NMR signals for similar intermediates were also observed for the reaction of depp **3** with both i-$PrCl_2$ and *t*-$BuPCl_2$, of dcxpp **4** with *n*-$PrPCl_2$, and of dippp **12** with *t*-$BuPCl_2$. In these systems, however, the cyclic product was not detected. The NMR data are given in Table 7. As all of these reactions involved quite bulky substituents on either the diphosphane and/or $R'PCl_2$, it seems probable that steric hindrance can prevent ring formation in unfavourable cases.

Five of the compounds, **1c**, **1d**, **6c**, **6e** and **11c**, have been isolated as solids, and their crystal and molecular structures have been determined at 120 K. The molecular structures of **1c** and **1d** are shown in Fig. 1 and 2 respectively. In both cases, the counter-ions to the dication are one Cl^- and one $AlCl_4^-$. Selected bond distances and angles for all the new structures are listed in Table 8. The most significant bond lengths in **1c** are the P–P distances, which are 2.2108(9) and 2.2327(9) Å. These values, as expected, lie in the range for normal P–P single bonds. The P–P–P angle is 90.30(3)°.

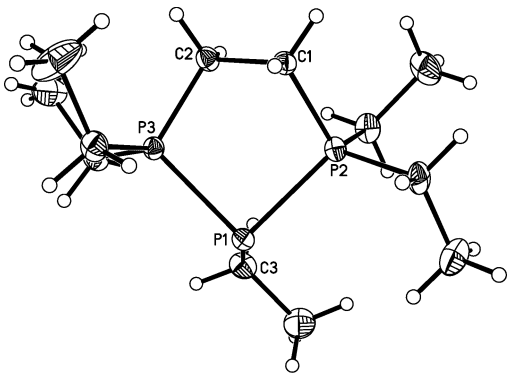


Fig. 1 The molecular structure of the dication **1c**, showing the numbering scheme for the key atoms (the counter-ions have been omitted for clarity). Thermal ellipsoids are drawn at 50% probability.

Table 8 Selected inter-atomic distances and angles

Compound	P–P/Å		P–P–P/°	P^a–C/Å
1c	2.2327(9)	2.2108(9)	90.30(3)	1.864(3)
1d	2.2302(8)	2.2105(8)	90.06(3)	1.867(2)
6c	2.225(3)	2.201(3)	89.17(12)	1.848(10)
	2.218(3)	2.203(3)	89.41(11)	1.867(9)
6e	2.231(3)	2.220(3)	86.09(11)	1.880(8)
11c	2.214(3)	2.197(4)	96.59(13)	1.867(9)

[a] Central P, shown as P_C in Scheme 5.

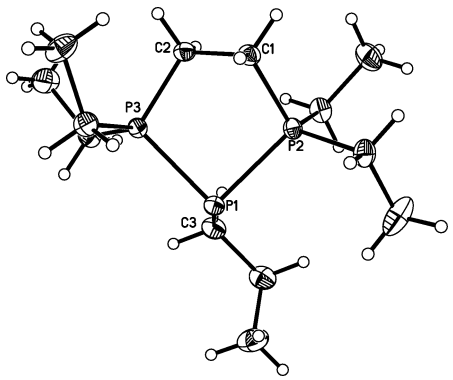


Fig. 2 The molecular structure of the dication **1d** (the counter-ions have been omitted for clarity). Thermal ellipsoids are drawn at 50% probability.

Very similar parameters are obtained for **1d**; the P–P bond lengths are 2.2105(8) and 2.2302(8) Å, while the P–P–P angle is 90.06(3)°. In **6c**, both counter-ions are $AlCl_4^-$; its molecular structure is shown in Fig. 3. The P–P distances are very similar, at 2.201(3)–2.225(3) Å, and the P–P–P angles are slightly smaller at 89.17(12) and 89.41(11)° (Table 8). The crystals of **6e** were obtained from a reaction carried out with $SnCl_2$ rather than $AlCl_3$ present, the counter-ion being $SnCl_6^{2-}$ in this complex (Fig. 4). In these crystals there are also two $CDCl_3$ molecules of crystallisation. The $SnCl_6^{2-}$ ion is not expected to form during the synthesis of **6e** itself, but from a parallel reaction leading to the 4P derivative,[14] as mentioned earlier. In this structure, one of the carbon atoms linking the two PPh_2 groups, one of the P atoms coordinated to it and one of the phenyl groups attached to the latter were disordered over two positions, with refined occupancies of 89.2(7)

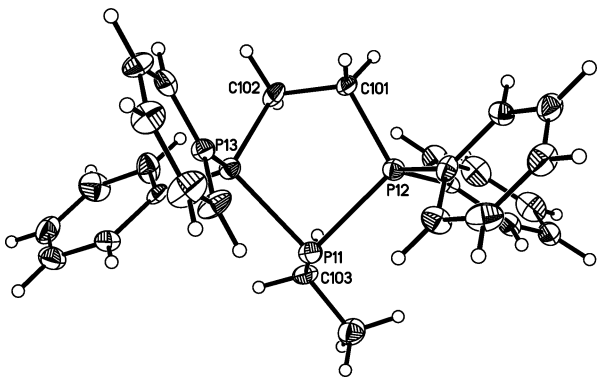


Fig. 3 The molecular structure of the dication **6c** (only one dication is shown and the counter-ions have been omitted for clarity). Thermal ellipsoids are drawn at 50% probability.

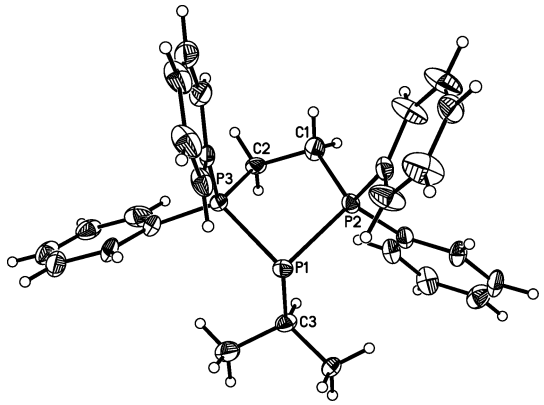


Fig. 4 The molecular structure of the dication **6e** (the counter-ion, disordered component and solvent molecules have been omitted for clarity). Thermal ellipsoids are drawn at 50% probability.

and 10.8(7)% respectively (see the Experimental section). The P–P bond distances of 2.231(3) and 2.220(3) Å in the major component are again entirely commensurate with P–P single bonds. The P–P–P bond angle is rather smaller at 86.09(11)°, probably because of the steric effect of the larger i-Pr instead of an Et group on the central phosphorus atom. The molecular structure of compound **11c**, with a seven-membered ring, is shown in Fig. 5. The counter-ion in this salt is $SnCl_6^{2-}$. The bond lengths of 2.214(3) and 2.197(4) Å again correspond to P–P single bonds; the P–P–P bond angle of 96.59(13)° reflects the difference in ring size from the other four structures.

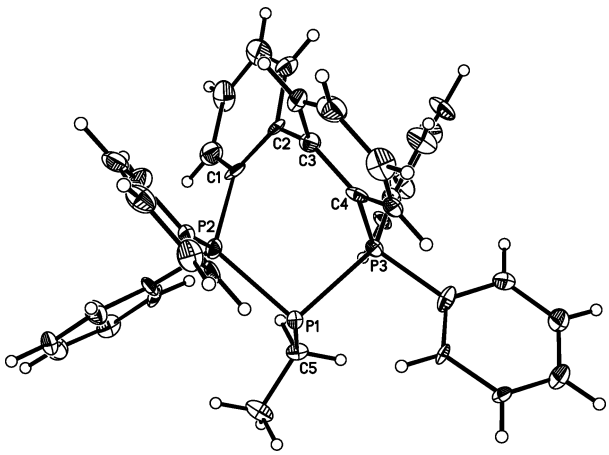


Fig. 5 The molecular structure of the dication **11c** (the counter-ions and solvent molecules have been omitted for clarity). Thermal ellipsoids are drawn at 50% probability.

In all of the cyclic triphosphenium ions which have been structurally characterised, the P–P distances lie between 2.1172(7) and 2.135(2) Å, attributed to a delocalised system, and a bond order higher than one for both P–P bonds.[1–9] This possibility is removed by oxidation, and the bond lengths in the di-ium dications are exactly as expected for single P–P bonds. We predict with some confidence that further structural studies on cyclic triphosphenium ions and on their alkyl- or aryl-substituted derivatives will give comparable results to those obtained in previous studies for the former, and in the present work for the latter, with a likely range between 2.19 and 2.24 Å for the single-bonded systems.

Conclusions

We therefore conclude that many examples of the di-ium dications should be preparable, although the scope for direct attack on the central phosphorus atom of a cyclic triphosphenium ion seems quite limited, because of steric constraints. It may also be difficult for cyclisation to occur in the alternative synthetic route when both R′ and R are bulky. The ions seem quite stable once formed, and X-ray crystallographic studies have confirmed the presence of P–P single bonds with the change of formal oxidation state of the central atom from P(I) to P(III).

Experimental

All manipulations, including NMR sample preparation, were carried out either under an inert atmosphere of dry nitrogen or *in vacuo*, using standard Schlenk line or glovebox techniques. 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, to verify that no major impurities were present. ^{31}P NMR spectra were obtained on Varian Unity 300, Mercury 400 or Inova 500 Fourier-transform spectrometers at 121.40, 161.91 or 202.3 MHz respectively; chemical shifts are referenced to 85% H_3PO_4, with the high frequency direction taken as positive.

Direct methylations using excess methyl triflate were carried out as described previously.[10,11] For the direct ethylation reactions, the cyclic triphosphenium ion **1a** was prepared in $CDCl_3$ solution from depe **1** (0.0959 g, 0.46 mmol) and PCl_3 (0.03 ml, 0.31 mmol); after verification that the ion **1a** had formed, ethyl triflate (0.08 ml, 0.62 mmol) was added by syringe. Cyclic triphosphenium ion **3a** was similarly prepared from depp **3** (0.0955 g, 0.43 mmol) and PCl_3 (0.03 ml, 0.31 mmol); after formation of **3a**, excess ethyl triflate (0.12 ml, 0.93 mmol) was added. The indirect alkylations or arylations were performed by mixing solutions of the diphosphane, the dichlorophosphane and $AlCl_3$ or $SnCl_2$ in $CDCl_3$ as solvent. In a typical preparation of **7e**, solutions of dcxpm **7** (0.0369 g, 0.09 mmol), i-PrPCl$_2$ (0.02 ml, 0.16 mmol) and $AlCl_3$ (0.0240 g, 0.18 mmol) were mixed. The same dication **7e** was prepared in the presence of $SnCl_2$ from solutions of dcxpm **7** (0.0319 g, 0.08 mmol), i-PrPCl$_2$ (0.02 ml, 0.16 mmol) and $SnCl_2$ (0.0303 g, 0.16 mmol) in $CDCl_3$. All other compounds were prepared in a similar manner. Some of the solution in each case was set aside in a crystal tube to see whether crystals would form. Crystals suitable for X-ray diffraction were obtained from solutions of **1c**, **1d** and **6c** where $AlCl_3$ was used as the chloride acceptor, while crystals of **6e** and **11c** were obtained as hexachlorostannate(IV) salts from similar reactions with $SnCl_2$ present. The formation of a tin(IV) species showed that a redox reaction, probably leading to a tetraphosphonium dication (4P)[14], had occurred in these systems.

X-Ray crystallography

Single crystal structure determinations were carried out from data collected using graphite monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) on a Bruker SMART-CCD 1K diffractometer at 120 K. The temperature was controlled using a Cryostream N_2 flow cooling device.[15] In each case, series of narrow ω-scans (0.3 °) were performed at several ϕ-settings in such a way as to cover a sphere

of data to a maximum resolution of 0.70 Å. Cell parameters were determined and refined using SMART software,[16] and raw frame data were integrated using the SAINT program.[17] The structures were solved using direct methods,[18] and refined by full-matrix least-squares on F^2 using SHELXL-97[19] and the graphical user interface Olex2[20] or CRYSTALS.[21] For **6c** reflection intensities were corrected by numerical integration based on measurements and indexing of the crystal faces using the SHELXTL software.[22] In the remaining cases, intensities were corrected for absorption effects by the multi-scan method, based on multiple scans of identical and Laue equivalent reflections (using the SADABS software).[23] In general, non-hydrogen atoms were refined with anisotropic displacement parameters and hydrogen atoms were positioned geometrically and refined using a riding model. In the structure of **6e**, restraints were necessary during the refinement of one of the C–PPh_2 moieties. The carbon atom, the P atom coordinated to it and one of its attached phenyl rings were modelled as disordered over two positions (refined occupancies of 89.2(7) and 10.8(7)% respectively). Each pair of disordered atoms was constrained to have the same displacement parameters. Distances between equivalent atoms in the disordered section with lower occupancy were restrained to be the same as those from the fragment with higher occupancy. In addition, the anisotropic displacement parameters of all carbon atoms belonging to the phenyl rings were subject to a 'rigid body' restraint. The distance between P1 and the minor component P3A was restrained to a sensible distance. The diffraction data for **11c** were also of poor quality, so similar-ADP and rigid bond restraints were used to maintain sensible geometries.

Single crystal data for 1c. $M_r = 470.49$, monoclinic, Cc, $Z = 4$, $a = 10.1314(4)$ Å, $b = 25.1148(11)$ Å, $c = 8.8636(4)$ Å, $\beta = 90.957(1)°$, $V = 2255.01(17)$ Å, data/restraints/parameters 5601/2/196 ($R_{int} = 0.0266$), final $R_1 = 0.0359$, $wR_2 = 0.0789$ ($I>2\sigma(I)$).

Single crystal data for 1d. $M_r = 484.52$, monoclinic, Cc, $Z = 4$, $a = 10.3722(3)$ Å, $b = 25.1650(8)$ Å, $c = 8.8229(3)$ Å, $\beta = 90.502(1)°$, $V = 2302.83(13)$ Å, data/restraints/parameters 7542/2/205 ($R_{int} = 0.0302$), final $R_1 = 0.0331$, $wR_2 = 0.0742$ ($I>2\sigma(I)$).

Single crystal data for 6c. $M_r = 796.05$, orthorhombic, $Pba2$, $Z = 4$, $a = 22.8830(16)$ Å, $b = 31.806(2)$ Å, $c = 9.8121(7)$ Å, $V = 7141.4(8)$ Å, data/restraints/parameters 14723/1/741 ($R_{int} = 0.098$), final $R_1 = 0.0695$, $wR_2 = 0.1120$ ($I>2\sigma(I)$).

Single crystal data for 6e. $M_r = 1042.57$, monoclinic, $P2_1/n$, $Z = 4$, $a = 12.7862(8)$ Å, $b = 21.2600(14)$ Å, $c = 15.2904(10)$ Å, $\beta = 94.661(1)°$, $V = 4142.7(5)$ Å, data/restraints/parameters 7314/61/442 ($R_{int} = 0.0813$), final $R_1 = 0.0671$, $wR_2 = 0.1362$ ($I>2\sigma(I)$).

Single crystal data for 11c. $M_r = 1152.68$, triclinic, $P\bar{1}$, $Z = 2$, $a = 10.7742(10)$ Å, $b = 11.4878(10)$ Å, $c = 19.2490(17)$ Å, $\alpha = 89.558(2)°$, $\beta = 82.088(2)°$, $\gamma = 82.033(2)°$, $V = 2336.9(4)$ Å, Data/restraints/parameters 9111/299/509 ($R_{int} = 0.1124$), final $R_1 = 0.0908$, $wR_2 = 0.1284$ ($I>2\sigma(I)$).

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