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PAPER

The relative stabilities of cyclic dicationic derivatives of diphosphanes with three (3P) or four (4P) linked phosphorus atoms†

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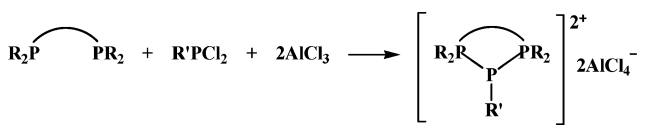
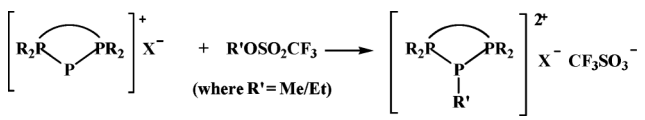
Reaction of a diphosphane with a chlorophosphane in the presence of $SnCl_2$ or $AlCl_3$ leads to the formation of dicationic heterocycles with three (3P) or four (4P) linked phosphorus atoms. Some 3P derivatives with small alkyl substituents may also be prepared by direct alkylation of cyclic triphosphenium ions. Several new species were prepared in solution, some of which were isolated and characterised by single-crystal X-ray diffraction. Investigations into the factors favouring formation of 3P or 4P species are described.

Introduction

The synthesis of the first two dicationic phosphorus heterocycles with three linked phosphorus atoms (3P) was described by Schmidpeter and co-workers, by reaction of a diphosphane with a halophosphane in the presence of $AlCl_3$ (Scheme 1).[1] These compounds may also be prepared by direct alkylation of cyclic triphosphenium ions (CTIs) on the central (bare) phosphorus atom, at least for small R′ groups (Scheme 2).[2,3] In a recent paper, we described the synthesis by these two routes of several new 3P compounds, five of which were characterised by single-crystal X-ray diffraction.[3]

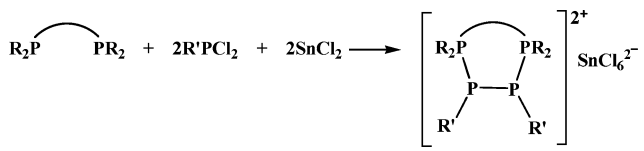


Scheme 1 The synthesis of P-alkylated cyclic triphosphenium ions (3P).



Scheme 2 Direct alkylation of a CTI.

We have also shown in a preliminary communication that it is sometimes possible to add a second R′PCl_2 molecule to a diphosphane to yield a cyclic tetraphosphonium dication with four linked phosphorus atoms (4P), Scheme 3; the crystal and molecular structures of two of these compounds were determined.[4] These reactions were initially carried out in the presence of $SnCl_2$, since a redox reaction is a necessary stage in the process. A further reaction leading to both 3P and 4P products has subsequently been described by Weigand, Burford and co-workers, and the molecular structure of their 3P dication was elucidated.[5] In all instances, for both 3P and 4P species, the P–P bond distances are as expected for single bonds.



Scheme 3 The synthesis of cyclic tetraphosphonium ions (4P) with $SnCl_2$.

In the present work, the syntheses of several new 3P and 4P dications are described, some of which were characterised crystallographically. The factors favouring formation of 3P or 4P species in these often competing reactions are discussed.

Results and discussion

(a) New 3P dications

The ^{31}P solution-state NMR data for the new 3P species, Fig. 1, are shown in Table 1, including examples of ring sizes from 4–8. Compounds **1–7** (Fig. 1) were synthesised by the route shown in Scheme 1 in the presence of $AlCl_3$ or $SnCl_2$,[1,3] whereas dications

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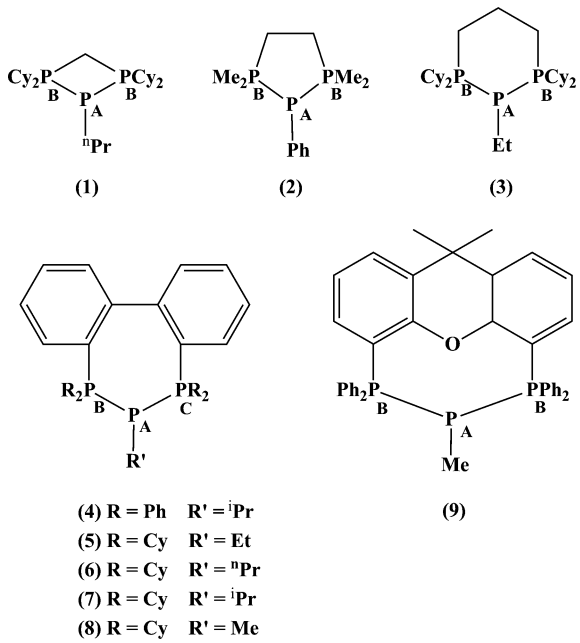
Table 1 ^{31}P NMR data for P-alkylated cyclic triphosphenium ions

Diphosphane	R′	Ring size	P_B, ppm	P_C, ppm	P_A, ppm	$^1J_{P\text{-}P}$, Hz	Counter-ion
dcypm (**1**)	^{n}Pr	4	41.4	—	−64.0	159	$AlCl_4^-$
dmpe (**2**)	Ph	5	46.6	—	−76.4	290	$AlCl_4^-$
dcypp (**3**)	Et	6	28.7	—	−92.4	303	$[Al_2O_4Cl_{10}]^{2-}$
biphep (**4**)	^{i}Pr	7	17.3	12.5	−12.2	310, 324	$SnCl_6^{2-}$
cybiphep (**5**)	Et	7	25.2	24.3	−7.6	296, 317	$SnCl_6^{2-}$
cybiphep (**6**)	^{n}Pr	7	25.5	24.7	−13.5	296, 319	$SnCl_6^{2-}$
cybiphep (**7**)	^{i}Pr	7	25.2	24.3	−7.3	297, 318	$SnCl_6^{2-}$
cybiphep (**8**)	Me	7	24.1	20.2	−24.9	292, 301	$SnCl_6^{2-}$/triflate
dppdmx (**9**)	Me	8	21.8	—	−10.1	362	$SnCl_6^{2-}$/triflate



(4) R = Ph R′ = ^{i}Pr
(5) R = Cy R′ = Et
(6) R = Cy R′ = ^{n}Pr
(7) R = Cy R′ = ^{i}Pr
(8) R = Cy R′ = Me

Fig. 1 The 3P dications synthesised (all carry a 2+ charge).

8 and **9** were prepared by direct methylation using methyl triflate of the corresponding cyclic triphosphenium ion (Scheme 2).[2,3] For biphep and cybiphep derivatives only, the outer phosphorus atoms P_B and P_C are inequivalent, so the P_A resonance appeared as a doublet of doublets (Table 1). In all instances, the $^1J_{PP}$ values are appreciably smaller than those in the corresponding cyclic triphosphenium ions, with no substituent on P_A.[2–4,6–17]

Dications **1**, **3** and **6** were isolated in crystalline form with counter-ions $AlCl_4^-$, $[Al_4O_2Cl_{10}]^{2-}$[18–24] and $SnCl_3^-$ + $\frac{1}{2}SnCl_6^{2-}$, respectively, and were studied by low-temperature single-crystal X-ray diffraction. Unfortunately, due to the very air-sensitive nature of **1**, the quality of the data obtained was such that while the connectivities and basic structure could be ascertained, reliable bond length and bond angle values could not be determined. Nevertheless, the four-membered ring structure was unequivocally confirmed. **3** represents the first example of a six-membered ring dication of this type to be structurally characterised; its molecular structure is shown in Fig. 2. As found previously in both larger and smaller rings,[3] the P–P distances (Table 2) are entirely as expected for single bonds, while the P_B–P_A–P_B bond angle is larger at 102.95(8)° than in either the 5- or 7-membered ring examples.[3]

6 is a new type of 7-membered ring system and its molecular structure is illustrated in Fig. 3. The counter-ions are $SnCl_3^-$ and $\frac{1}{2}SnCl_6^{2-}$ and there are also four $CDCl_3$ molecules in the asymmetric unit, two of which show some disorder. P–P bond distances (Table 2) are again entirely compatible with single bonds, while the P_B–P_A–P_C bond angle of 97.72(8)° is comparable to that of 96.59(13)° found in the only previous structurally characterised 7-membered ring dication of this type.[3]

Table 2 Selected bond distances and angles for compounds **3** and **6**

	3	**6**
P1–P2 (Å)	2.199(2)	2.231(2)
P1–P3 (Å)	2.202(2)	2.208(2)
P^P^P(°)	102.95(8)	97.72(8)
P1–C (Å)	1.807(6)	1.863(6)

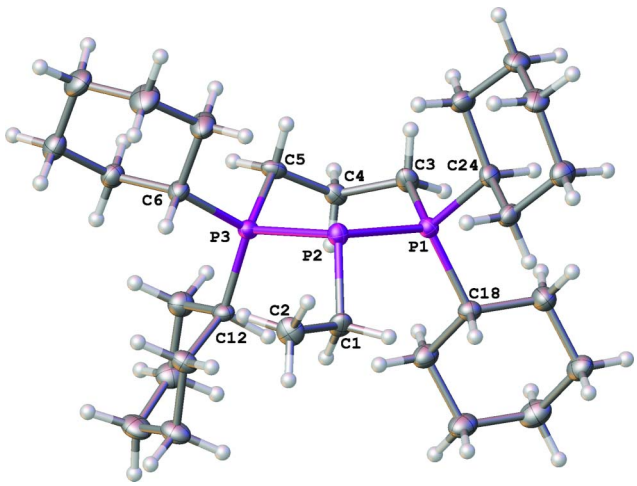


Fig. 2 The molecular structure of dication **3**, showing the numbering scheme for the key atoms (only the major component is shown and the counter-ions have been omitted for clarity). Atomic Displacement Parameters (ADPs) are drawn at 50% probability.

Table 3 contains the ^{31}P solution-state NMR spectroscopic data for five examples of 3P dications with a different counter-ion from those described in earlier work.[2,3] In all instances, there is good agreement between the sets of NMR parameters for each of the dications, showing that a change of anion is not a major influence on these values. This parallels the behaviour of cyclic triphosphenium ions, where a change of anion has little effect on the ^{31}P chemical shifts of the cation.[2,6,7,10–16,25]

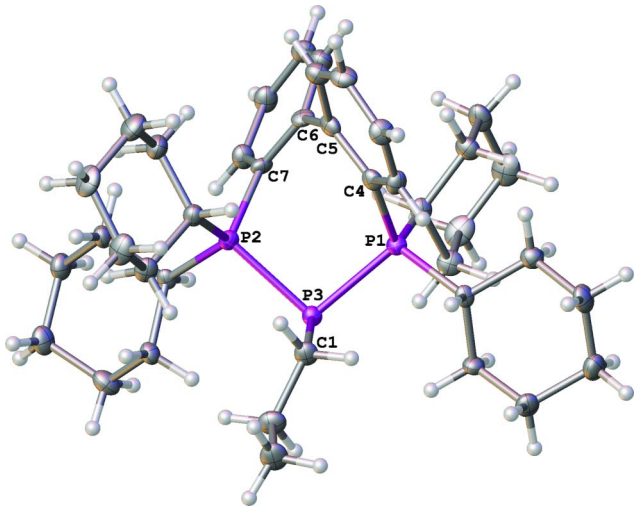


Fig. 3 The molecular structure of the dication **6**, showing the numbering scheme for the key atoms (the counter-ions have been omitted for clarity). ADPs are drawn at 50% probability.

Table 3 ^{31}P NMR spectroscopic data for alkylated cyclic triphosphenium ions with different counter-ions to those described previously[2,3]

Diphosphane	R	Ring size	P_B, ppm	P_A, ppm	$^1J_{P-P}$, Hz	Counter-ion
dcypm (**10**)	Et	4	39.5	–62.8	157	$SnCl_6^{2-}$
dppe (**11**)	Et	5	53.6	–96.2	299	$SnCl_6^{2-}$
dppe (**12**)	^{t}Bu	5	50.2	–54.2	336	$SnCl_6^{2-}$
dppe (**13**)	Ph	5	52.8	–79.2	293	$SnCl_6^{2-}$
depp (**14**)	Et	6	29.3	–81.9	303	$SnCl_6^{2-}$

(b) New 4P dications

Previously, we reported that for the 4P product to be formed, a diphosphane, a chlorophosphane and tin(II) chloride were necessary, as without any one of these components no reaction takes place.[4] Here, we show that in the synthesis of 4P systems tin(II) chloride can be replaced with aluminium trichloride, with the diphosphane now acting as the reducing agent to allow formation of the 4P product. Use of diphosphanes as reducing agents has previously been demonstrated in the synthesis of cyclic triphosphenium ions.[7,10] Either the diphosphane tetrachloride (Scheme 4a) or dichloride (Scheme 4b) is a possible oxidation product; these may be readily distinguished by ^{31}P NMR spectroscopy, since the dichloride will give rise to a pair of doublets, whereas the tetrachloride will yield a single peak only.

Compounds **15–25** (Fig. 4) were synthesised by the route shown in Scheme 3, using either $AlCl_3$ or $SnCl_2$. As we have previously reported, these 4P systems are readily identifiable by ^{31}P NMR spectroscopy, as they give rise to an AA′XX′ pattern.[4] The ^{31}P NMR spectroscopic data for compounds **15–25** were analysed directly from the spectra, as described by Günther,[26] and the results are presented in Table 4. The coupling constants for these systems are in good agreement with those previously reported for 4P systems[4,5] and for other compounds containing four- or six-linked phosphorus atoms.[27,28] In a few instances (**15b**, **17b**, **19a**,

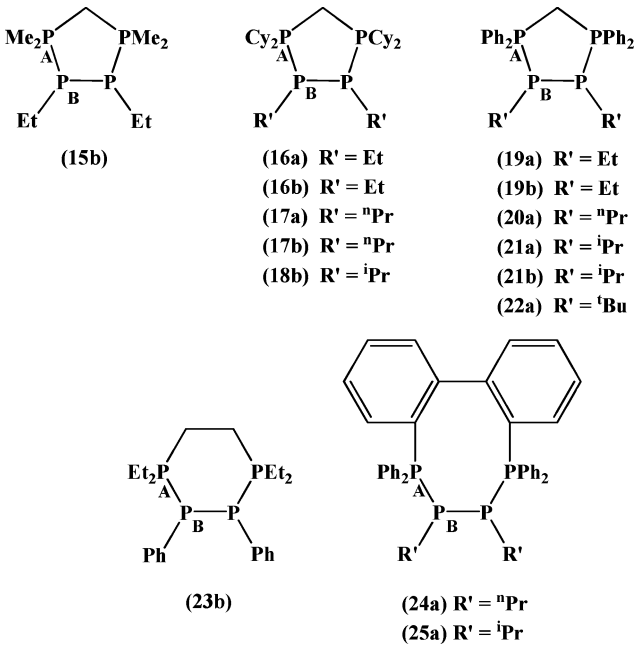


Fig. 4 The 4P dications synthesised (all carry a 2+ charge; counter-ions: a denotes $SnCl_6^{2-}$; b denotes $AlCl_4^-$).

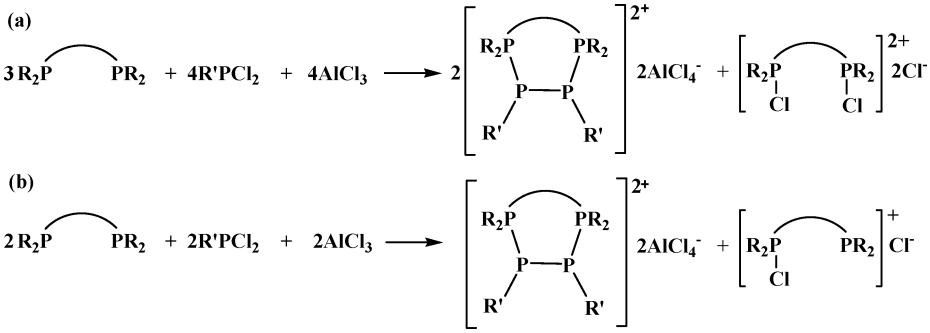
Table 4 ^{31}P NMR spectroscopic data for 4P systems[a]

Diphosphane	*R*	Ring size	P_B, ppm	P_A, ppm	$^1J_{AB}$, Hz	$^1J_{BB'}$, Hz	$^2J_{AB'}$, Hz	$^3J_{AA'}$, Hz	Counter-ion
dmpm (**15b**)	Et	5	–38.3	62.1	—	—	—	—	$AlCl_4^-$
dcypm (**16a**)	Et	5	–51.6	54.4	290	203	–36	36	$SnCl_6^{2-}$
dcypm (**16b**)	Et	5	–51.9	54.4	288	202	–36	34	$AlCl_4^-$
dcypm (**17a**)	^{n}Pr	5	–49.2	54.0	241	241	–49	8	$SnCl_6^{2-}$
dcypm (**17b**)	^{n}Pr	5	–48.5	57.2	—	—	—	—	$AlCl_4^-$
dcypm (**18b**)	^{i}Pr	5	–37.9	51.8	306	306	–41	46	$AlCl_4^-$
dppm (**19a**)	Et	5	–40.8	57.5	357	175	–30	74	$SnCl_6^{2-}$
dppm (**19b**)	Et	5	–41.9	55.3	384	280	–56	58	$AlCl_4^-$
dppm (**20a**)	^{n}Pr	5	–48.7	58.1	—	—	—	—	$SnCl_6^{2-}$
dppm (**21a**)	^{i}Pr	5	–26.2	51.7	—	—	—	—	$SnCl_6^{2-}$
dppm (**21b**)	^{i}Pr	5	~ –31	~ 40	—	—	—	—	$AlCl_4^-$
dppm (**22a**)	^{t}Bu	5	4.2	44.7	339	287	–9	15	$SnCl_6^{2-}$
depe (**23b**)	Ph	6	–71.1	31.5	307	140	–30	–3	$AlCl_4^-$
biphep (**24a**)	^{n}Pr	8	–59.8	30.8	318	125	–80	11	$SnCl_6^{2-}$
biphep (**25a**)	^{i}Pr	8	–41.8	30.3	321	141	–88	15	$SnCl_6^{2-}$

[a] Labels A and B relate to the structures in Fig. 4 and have no relation to the description of the spin system as AA′XX′.

Table 5 ^{31}P NMR spectroscopic data for diphosphane dichlorides and related compounds

Diphosphane dichloride	P_A, ppm	P_B, ppm	$^2J_{P\text{-}P}$, Hz	Chloro-cation	P, ppm	Ref.	Diphosphane	P, ppm	Ref.
$Me_2P_A(Cl)CH_2P_BMe_2$	96.5	–47.6	72	Me_3PCl^+	90.0	29	$Me_2PCH_2PMe_2$	–53.5	2
$Cy_2P_A(Cl)CH_2P_BCy_2$	108.0	–9.7	59	Cy_3PCl^+	104.2	30	$Cy_2PCH_2PCy_2$	–8.9	2
$Ph_2P_A(Cl)CH_2P_BPh_2$	73.5	–26.2	79	Ph_2EtPCl^+	78.1	30	$Ph_2PCH_2PPh_2$	–20.4	



Scheme 4 The synthesis of cyclic tetraphosphonium ions (4P) with $AlCl_3$.

20a, **21a** and **21b**) the spectra were insufficiently well-resolved for a full analysis to be carried out.

In the $AlCl_3$ reactions, the formation of **15b**, **16b**, **17b**, **18b**, **19b** and **21b** was accompanied by the diphosphane dichloride (Scheme 4b), since pairs of doublets were apparent in the ^{31}P NMR spectra, one at a higher frequency for the phosphorus bound to chlorine and one at a lower frequency near to the shift of the diphosphane itself. The results are given in Table 5, with average shifts and coupling constants for each of the diphosphane dichlorides. Data for similar species, both chloro-cations and diphosphanes, are included for comparison. For **23b** only, the tetrachloride formed (Scheme 4a), as shown by a single ^{31}P resonance at 108.2 ppm; this compares well with the value of 109.9 ppm reported previously for this compound.[7] We therefore conclude that under our conditions the preferred oxidation product of the diphosphane is the dichloride, except for depe, which may well be the most readily oxidised of these diphosphanes and leads to the tetrachloride.

Crystals suitable for X-ray diffraction of the dications **16b** and **19a** were obtained and their molecular structures determined at low temperature (Fig. 5 and 6, respectively). For each compound, selected bond distances and angles are presented in Table 6. The molecular structure of **16b** contains two $AlCl_4^-$ counter-ions and one molecule of $CHCl_3$ within the unit cell, whereas within the unit cell of **19a** there are two half molecules of $SnCl_6^{2-}$ as counter-ions for the dication and no solvent.

The molecular structure of a 4P dication derived from dppm, $EtPCl_2$ and $SnCl_2$ has previously been reported, where the unit cell contains one $SnCl_6^{2-}$ counter-ion for the dication and two molecules of $CHCl_3$.[4] **19a** is a solvatomorph of this literature compound, without the two $CHCl_3$ molecules; they show differences in the orientations of the substituents on the four phosphorus atoms, Fig. 7.

The P–P bond lengths in both **16b** and **19a** are typical values for normal P–P single bonds (Table 6) and are similar to those found in the 3P dications,[3] other 4P dications[4] and those reported for other compounds containing four linked phosphorus atoms.[31–37]

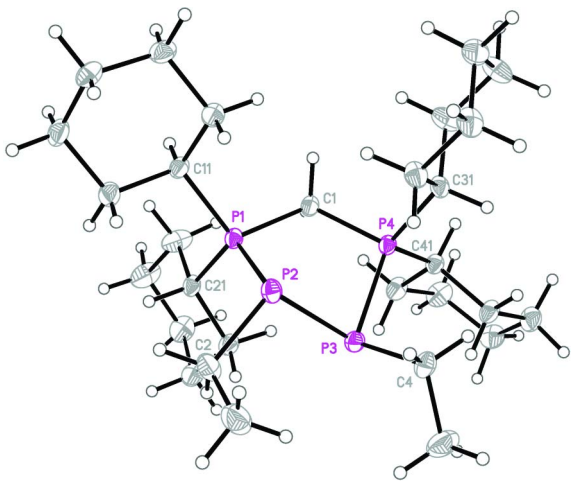


Fig. 5 The crystal and molecular structure of the dication **16b**. The two $AlCl_4^-$ counter-ions and $CHCl_3$ molecule have been omitted for clarity. ADPs are drawn at 50% probability.

Table 6 Selected bond distances and angles for compounds **16b** and **19a**

	16b	**19a**
P1–P2 (Å)	2.2055(17)	2.2056(14)
P2–P3 (Å)	2.2045(18)	2.2044(15)
P3–P4 (Å)	2.1904(17)	2.1907(15)
P2–C (Å)	1.790(5)	1.854(5)
P3–C (Å)	1.855(5)	1.872(5)
P1^P2^P3(°)	99.23(7)	99.27(6)
P2^P3^P4(°)	96.68(6)	96.69(5)

(c) Investigating the relative stabilities of 3P and 4P dications

3P and 4P dications are often formed in competing reactions. The proposed mechanism of formation for both 3P and 4P dications is shown in Scheme 5. The first step, attack of a phosphorus atom of the diphosphane on one $R'PCl_2$ molecule, is assumed to be identical for the formation of both 3P and 4P rings. For the 3P species to form, ring closure must then occur. Alternatively,

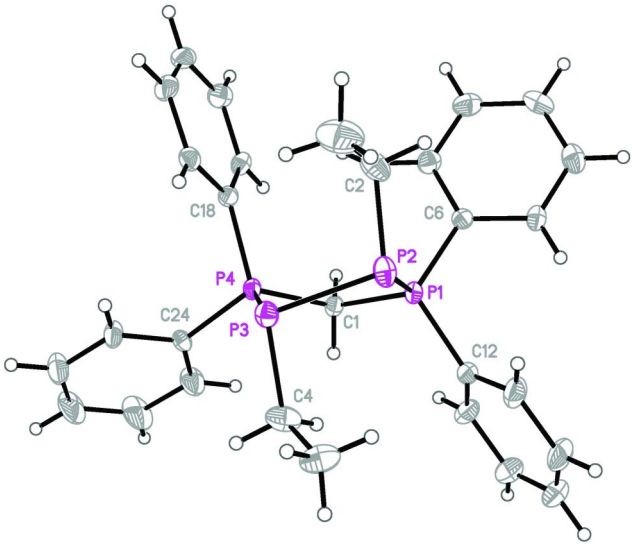


Fig. 6 The crystal and molecular structure of the dication **19a**. Only the major component is shown and the two half molecules of $SnCl_6^{2-}$ as counter-ions have been omitted for clarity. ADPs are drawn at 50% probability.

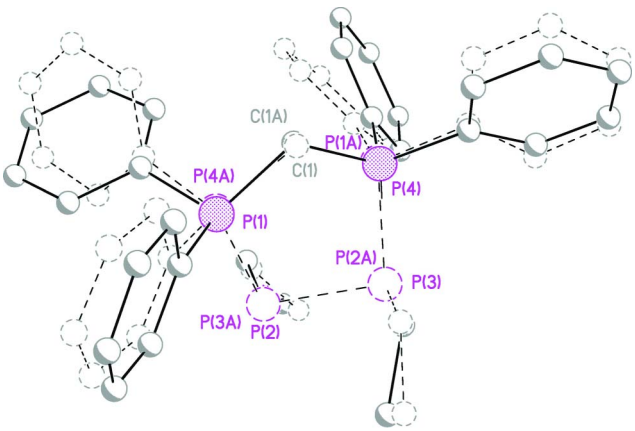


Fig. 7 Overlap of the dications **19a** and the previously reported solvatomorph.

addition of a second molecule of $R'PCl_2$ can take place (redox step) at the previously added phosphorus atom to afford an unsymmetrical monocationic intermediate, as shown previously by NMR studies.[4] Ring closure can then occur to afford the 4P dication.

In support of the proposed mechanism, the first intermediate **I** (Scheme 5) was detected by ^{31}P NMR spectroscopy from the reactions of dppm with $EtPCl_2$ and $^iPrPCl_2$ (Table 7). The NMR parameters are very similar to those reported previously for the acyclic intermediate in the formation of a 3P species,[7] though in the present case the 4P dication is preferentially formed. The main difference, however, is that ^2J and ^3J coupling are apparent in this instance because of the close proximity of the phosphorus atoms.

Table 8 Preferential formation of a 3P or 4P product

Diphosphane $R_2P(CH_2)_nPR_2$	3P ring size	4P ring size	Product
$n = 1$	4	5	4P preferred
$n = 2$	5	6	3P, 4P
$n = 3$	6	7	3P only
$n = 4$	7	8	3P, 4P

A marked preference is observed for formation of a 3P or 4P product, depending on relative ring size (Table 8). For a diphosphane where $n = 1$, giving rise to a 4-membered ring for the 3P dication or a 5-membered ring for the 4P dication, the latter is preferred, which is in keeping with normal stabilities for aliphatic or alicyclic rings. Where $n = 2$, both possible products are frequently seen, showing that both 5- and 6-membered rings are stable. When $n = 3$, we have never detected a 4P product under our experimental conditions, the 3P 6-membered ring clearly being more stable than the potential 4P 7-membered ring. With larger rings, however, a mixture of 3P and 4P dications is again found, suggesting that there is little difference in stability between 7- and 8-membered rings.

Conclusions

We have shown that the formation of new cyclic dications with three (3P) or four (4P) linked phosphorus atoms and a hydrocarbon backbone is possible in several systems, from reaction of a diphosphane $R_2P(CH_2)_nPR_2$ with one or two moles of a chlorophosphane $R'PCl_2$, in the presence of either $AlCl_3$ or $SnCl_2$ to act as a halide acceptor. Although the synthesis of 4P species involves a redox step, the presence of an additional reducing agent, such as $SnCl_2$, is not essential, since the diphosphane starting material may itself act as a reducing agent.

Formation of the 3P dication is favoured when a six-membered ring results and the corresponding 4P species has not been observed under our experimental conditions. The 4P derivative is favoured when its ring is five-membered, although some 3P analogues were detected under favourable conditions. For the cases where the 3P species is a five- or seven-membered ring, both 3P and 4P dications were detected in most instances, showing that their rings are of comparable stability. Direct alkylation of cyclic triphosphenium ions to form 3P dications is a feasible preparative route for small R′ groups only.

Table 7 ^{31}P NMR spectroscopic data for dppm intermediates (**I**) where R′ = Et or ^iPr

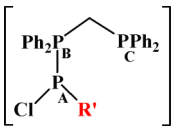
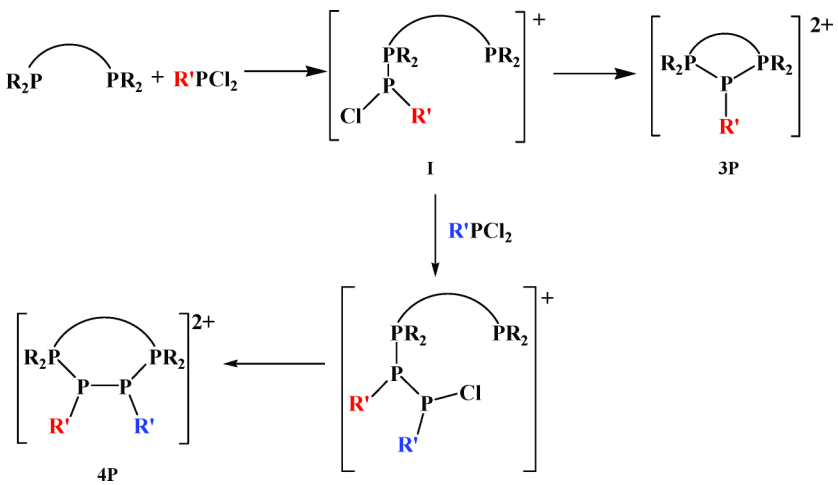
	R′	P_A, ppm	P_B, ppm	P_C, ppm	$^1J_{P\text{-}P}$, Hz	$^2J_{P\text{-}P}$, Hz	$^3J_{P\text{-}P}$, Hz
	Et	68.6	26.6	–27.8	329	66	87
	^iPr	79.4	25.2	–28.2	345	68	66

Table 9 Quantities of reagents used

Compound number	Diphosphane	R′ =	Quantity of diphoshane		Quantity of $R'PCl_2$		Quantity of $SnCl_2$		Quantity of $AlCl_3$	
			g	mmol	mL	mmol	g	mmol	g	mmol
1	dcypm	^{n}Pr	0.0394	0.10	0.013	0.10	—	—	0.0267	0.20
2	dmpe	Ph	0.0460	0.30	0.18	0.29	—	—	0.0816	0.61
3	dcypp	Et	0.0286	0.07	0.010	0.10	—	—	0.0187	0.14
4	biphep	^{i}Pr	0.0183	0.035	0.009	0.071	0.0113	0.060	—	—
5	cybiphep	Et	0.0092	0.017	0.004	0.038	0.0064	0.034	—	—
6	cybiphep	^{n}Pr	0.0139	0.025	0.007	0.051	0.0120	0.063	—	—
7	cybiphep	^{i}Pr	0.0196	0.036	0.004	0.032	0.0254	0.134	—	—
8	cybiphep	Me	0.0242	0.044	0.004[c]	0.046	0.014	0.073	0.020[b]	0.18[b]
9	dppdmx	Me	0.0300	0.052	0.020[c]	0.22	0.040	0.21	0.020[b]	0.18[b]
10	dcypm	Et	0.0497	0.12	0.030	0.28	0.0455	0.24	—	—
11	dppe	Et	0.1372	0.34	0.070	0.68	0.0906	0.68	—	—
12	dppe	^{t}Bu	0.0657	0.17	0.053	0.33	0.0449	0.34	—	—
13	dppe	Ph	0.3306	0.83	0.230	1.69	0.3204	1.69	—	—
14	depp	Et	0.0228	0.07	0.020	0.19	0.0265	0.14	—	—
15b	dmpm	Et	0.0268	0.20	0.020	0.22	—	—	0.0533	0.40
16a	dcypm	Et	0.0497	0.12	0.030	0.28	0.0325	0.24	—	—
16b	dcypm	Et	0.0419	0.10	0.010	0.10	—	—	0.0267	0.20
17a	dcypm	^{n}Pr	0.0360	0.09	0.028	0.27	0.0341	0.18	—	—
17b	dcypm	^{n}Pr	0.0394	0.10	0.013	0.10	—	—	0.0267	0.20
18b	dcypm	^{i}Pr	0.0402	0.10	0.012	0.10	—	—	0.0267	0.20
19a	dppm	Et	0.0503	0.13	0.030	0.28	0.0512	0.27	—	—
19b	dppm	Et	0.0645	0.17	0.050	0.51	—	—	0.0476	0.35
20a	dppm	^{n}Pr	0.0577	0.15	0.040	0.30	0.0569	0.42	—	—
21a	dppm	^{i}Pr	0.0462	0.12	0.030	0.33	0.0460	0.34	—	—
21b	dppm	^{i}Pr	0.0493	0.13	0.050	0.39	—	—	0.0356	0.26
22a	dppm	^{t}Bu	0.0307	0.08	0.0257[a]	0.16	0.0306	0.16	—	—
23b	depe	Ph	0.4037	1.96	0.270	1.96	—	—	0.5220	3.91
24a	biphep	^{n}Pr	0.0183	0.035	0.009	0.069	0.0137	0.072	—	—
25a	biphep	^{i}Pr	0.0183	0.035	0.009	0.071	0.0113	0.060	—	—

[a] $RPCl_2$ is a solid so the quantity is in g. [b] Quantity of methyl triflate used, not $AlCl_3$. [c] PCl_3 used, not $R'PCl_2$.



Scheme 5 The proposed mechanism of formation for 3P and 4P dications.

Experimental

Synthesis

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 (Saffron Scientific) 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 impurities were present. ^{31}P NMR spectra were obtained on a Varian Mercury 400 Fourier-transform spectrometer at 161.91 MHz; chemical shifts are referenced to 85% H_3PO_4, with the high frequency direction taken as positive.

Table 10 Crystallographic data

	3	6	16b	19a
Chemical formula	C29 H55 P3, 2(Al2 Cl5 O)	2(C39 H59 P3), Cl6 Sn, 8(C H Cl3), 2(Cl3 Sn)	C29 H56 P4, C H Cl3, 2(Al Cl4)	C29 H32 P4, Cl6 Sn
Formula weight	991.06	2975.87	985.55	835.82
Crystal system	triclinic	triclinic	monoclinic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$C2/c$	$P\bar{1}$
a/Å	10.6187(5)	10.5087(6)	38.5425(12)	10.5532(8)
b/Å	10.6364(5)	15.1261(8)	11.8925(4)	11.0978(8)
c/Å	21.8815(11)	20.8450(10)	26.5378(9)	16.1102(12)
α (°)	91.914(2)	72.928(2)	90	104.3190(10)
β (°)	94.314(2)	87.477(2)	130.3910(10)	92.3670(10)
γ (°)	111.132(2)	72.386(2)	90	100.4550(10)
Volume/Å^3	2293.80(19)	3015.3(3)	9264.6(5)	1790.4(2)
Z	2	1	8	2
Crystal size	0.06 × 0.12 × 0.14	0.17 × 0.17 × 0.19	0.27 × 0.38 × 0.42	0.15 × 0.15 × 0.20
Density/g cm^{-3}	1.435	1.638	1.413	1.550
μ/mm^{-1}	0.816	1.534	0.858	1.360
R_{int}	0.0778	0.0894	0.0760	0.0379
Data/restraints/ parameters	8111/1531/790	12391/6/607	12468/15/432	8782/0/375
R_1 [$I > 2\sigma(I)$]	0.0463	0.0520	0.0348	0.0466
wR_2 [$I > 2\sigma(I)$]	0.1031	0.1090	0.0882	0.1009
R_1 (all data)	0.0810	0.1113	0.0472	0.0666
wR_2 (all data)	0.1143	0.1301	0.0953	0.1085
Goodness of fit	0.944	0.981	1.017	1.037
$\Delta\rho_{min,max}$/e Å^{-3}	–0.775,0.763	–0.947,1.415	–0.860,0.966	–0.891,3.757

Example reactions are described below. All other reactions were carried out using similar methods. The quantities of reagents used are shown in Table 9. Crystals of **3**, **6**, **16b** and **19a** were obtained by slow evaporation of solvent in an inert atmosphere.

Example reactions

Synthesis of 3. $EtPCl_2$ (0.01 mL, 0.10 mmol) was added *via* syringe to a solution of dcypp (0.0286 g, 0.07 mmol) and $AlCl_3$ (0.018 g, 0.14 mmol) under a nitrogen atmosphere. A ^{31}P NMR spectrum was recorded soon after mixing.

Synthesis of 6. $EtPCl_2$ (0.007 mL, 0.051 mmol) was added *via* syringe to a solution of dcypm (0.0139 g, 0.025 mmol) and $SnCl_2$ (0.0120 g, 0.063 mmol) under a nitrogen atmosphere. A ^{31}P NMR spectrum was recorded soon after mixing.

Synthesis of 16b. $EtPCl_2$ (0.03 mL, 0.28 mmol) was added *via* syringe to a solution of dcypm (0.0419 g, 0.10 mmol) and $AlCl_3$ (0.026 g, 0.20 mmol) under a nitrogen atmosphere. A ^{31}P NMR spectrum was recorded soon after mixing.

Synthesis of 19a. **19a** was isolated from the attempted synthesis of a 'mixed' cyclic tetraphosphonium ion from reaction of dppm, $EtPCl_2$, ^{i}PrPCl$_2$ and $SnCl_2$. $EtPCl_2$ (0.01 mL, 0.11 mmol) was added *via* a syringe and ^{i}PrPCl$_2$ (0.01 mL, 0.11 mmol) was added *via* a second syringe to a stirring solution of dcypm (0.0497 g, 0.12 mmol) and $SnCl_2$ (0.032 g, 0.24 mmol) under a nitrogen atmosphere. A ^{31}P NMR spectrum was recorded soon after mixing.

Crystallography

Single crystal structure determinations were carried out from X-ray data collected at 120 K using graphite monochromated Mo-Kα radiation (λ = 0.71073 Å) on a Bruker SMART-CCD 1 K diffractometer. The temperature was controlled using an open flow N_2 Cryostream cooling device.[38] In each case, a series of narrow ω-scans (0.3°) was performed at several φ-settings to maximise data coverage. Cell parameters were determined and refined using the SMART software[39] and raw frame data were integrated using the SAINT program.[40] The structures were solved using direct methods[41] and refined by full-matrix least-squares on F^2 using SHELXTL[41] and the graphical user interface Olex2.[42] Crystallographic data for compounds **3**, **6**, **16b** and **19a** are listed in Table 10. Details of each refinement are given in the crystallographic information file, including treatment of disorder in compounds **3** and **19a**.

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