Medium-ring diphosphines from diphosphabicyclo[*k.l*.0]alkanes: stereoselective syntheses, structure and properties

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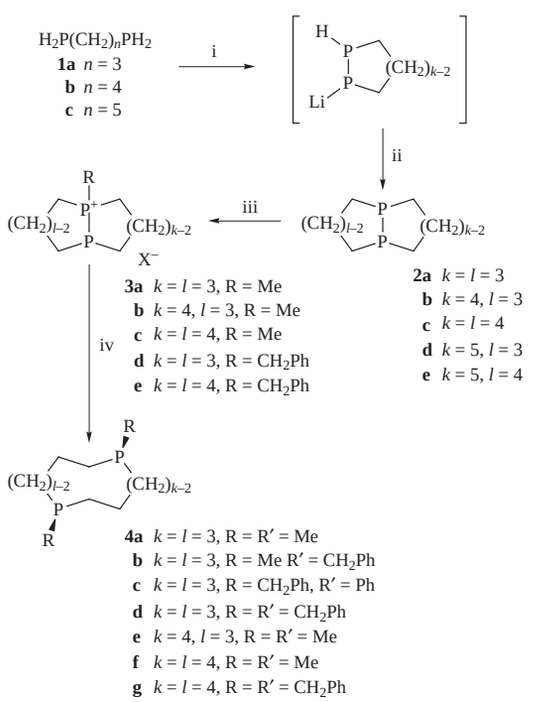
A series of 1,*k* + 2-diphosphabicyclo[*k.l*.0]alkanes 2b–e are prepared by Bu^{n}Li-promoted cyclisation of 1,ω-diphosphinoalkanes, followed by alkylation and cycloalkylation with 1,ω-dihaloalkanes. These compounds appear to be exclusively *cis*-isomers except 1,6-diphosphabicyclo[5.4.0]undecane 2e which is a 3:1 *cis*/*trans* mixture. Mono-quaternisation of *cis*-1,*k* + 2-diphosphabicyclo[*k.l*.0]alkanes, followed by treatment of the mono-quaternary salts with alkyllithium or Grignard reagents produces *cis*-1,*n*-disubstituted-1,*n*-diphosphacycloalkanes 4 exclusively; examples containing 8-, 9- and 10-membered rings and a range of substituents on phosphorus are described. Di-quaternisation of 1,*k* + 2-diphosphabicyclo-[*k.l*.0]alkanes, followed by hydrolysis, yields the *trans*-isomers of 1,*n*-disubstituted-1,*n*-diphosphacycloalkane monooxides 6 exclusively; reduction of these with $LiAlH_4$ in benzene gives largely *trans*-1,*n*-disubstituted-1,*n*-diphosphacycloalkanes 7, but is not completely stereoselective. The structure and properties of these diphosphacycloalkanes are discussed. He(I) photoelectron spectra of 1,5-diphosphabicyclo[3.3.0]octane, 1,6-diphosphabicyclo[4.3.0]nonane and 1,6-diphosphabicyclo[4.4.0]decane show little evidence of interaction between phosphorus lone pairs, unlike the corresponding hydrazines. The medium-ring diphosphacycloalkanes, 1,5-dimethyl-1,5-diphosphacyclooctane and 1,6-dimethyl-1,6-diphosphacyclodecane also show little evidence of interaction between phosphorus lone pairs.

Diphosphines in which the two phosphorus atoms are linked by a C_1–C_4 chain are extremely important chelating ligands in organometallic chemistry, and a wide variety of structures have been developed. Cyclic diphosphines in which the two phosphine lone pairs are *cis* could also be useful chelating ligands, potentially providing tighter control on lone pair orientation, and thus on chelating properties, but synthetic routes to these compounds are relatively undeveloped and the compounds are obtained as mixtures of stereoisomers, sometimes separable by chromatography. Known compounds include *P*,*P*-diphenyl derivatives of 1,4-diphospha-cyclohexane[1] and -cycloheptane,[1] and 1,5-diphosphacyclooctane.[1,2,3] An ingenious stereoselective synthesis of 1,5,9-triphosphacyclododecane and tertiary derivatives has recently been reported in which the triphosphine is created around a metal template.[4]

As part of our investigation of the intrabridgehead chemistry[5] of diphosphines,[6] we have developed novel synthetic routes to medium-ring diphosphines containing 8-, 9- and 10-membered rings and a range of substituents on phosphorus *via* diphosphabicycloalkanes.[7–9] This approach permits the preparation of pure *cis*-isomers which are potentially valuable chelating ligands; we have also developed a slightly less stereoselective route to the corresponding *trans*-isomers. The details of these preparations are described in this paper, along with the structure and properties of the compounds.



Scheme 1 *Reagents and conditions*: i Bu^{n}Li, $-H_2$; ii $Br(CH_2)_nCl$, Bu^{n}Li; iii RX; iv R′Li or R′MgBr

Results and discussion

Synthetic routes

The stereoselective route to pure *cis*-1,*n*-disubstituted-1,*n*-diphosphacycloalkanes **4a**–**g** is shown in Scheme 1. The scope of these reactions are discussed later; the observed stereochemistry depends on (i) formation of *cis*-isomers of 1,*k* + 2-diphosphabicyclo[*k.l*.0]alkanes **2** during cycloalkylation of monocyclic diphosphines and (ii) stereoselective P–P bond cleavage during reaction of mono-quaternised 1,*k* + 2-diphosphabicyclo[*k.l*.0]alkanes with alkyllithium or Grignard reagents.

The configuration of the 1,*k* + 2-diphosphabicyclo[*k.l*.0]-alkanes **2** is established in three cases (a) the disulfide derived from **2a** has been reported[10] to be *cis*, (b) X-ray structure determination of the disulfide derived from **2b** shows it to be

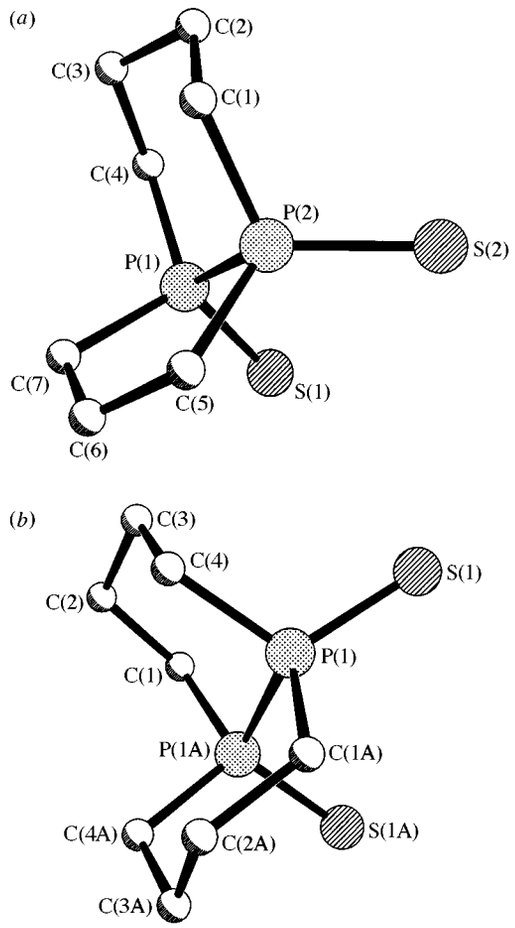


Fig. 1 X-Ray structure of (*a*) the disulfide of 1,6-diphosphabicyclo-[4.3.0]nonane **2b.S$_2$** and (*b*) the disulfide of 1,6-diphosphabicyclo-[4.4.0]decane **2c.S$_2$**

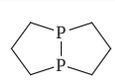
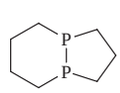
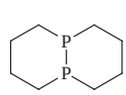
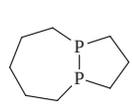
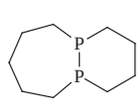
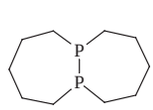
cis [Fig. 1(*a*)] and (c) we have reported[7] the *cis*-structure of **2c**; the X-ray structure of the disulfide of **2c** is shown in Fig. 1(*b*). In view of the calculations reported below and the ^{31}P chemical shifts, we believe all the compounds are *cis*, with the exception of the minor isomer of **2e**. Selected bond lengths and angles for the structures **2b.S$_2$** and **2c.S$_2$** are given in Table 1. In these structures the P–P distances are close to 2.20 Å, that for **2b.S$_2$** being marginally longer than that for **2c.S$_2$**, possibly as a consequence of ring strain (see below). The P=S distances are all about 1.94 Å, the P–C are 1.81 Å and the (ordered) C–C distances are *ca*. 1.52 Å. The effects of ring strain are most notable on the P–P–C angles of the 5-membered ring in **2b.S$_2$** which are *ca*. 93.5°, other angles at both P and S being closer to tetrahedral values.

The cycloalkylations which form the 1,k + 2-diphosphabicyclo[k.l.0]alkanes are undoubtedly kinetically-controlled, but the equilibrium preferences for *cis*- *versus* *trans*-isomers merits consideration first. A predicted strong preference for the *cis*-isomer of 1,6-diphosphabicyclo[4.4.0]decane was discussed in our preliminary communication,[7] and was ascribed to easier accommodation of the long P–P bond in the *cis*- relative to the *trans*-isomer. This preference appears to be general according to semi-empirical PM3 calculations on the other ring systems (Table 2). Semi-empirical methods like PM3 are ineffective for conformational searching but the MM2 force field is not parameterised for P–P bonds, so the following procedure was used to locate preferred conformations. The corresponding 1,k + 2-disilabicyclic[k.l.0]alkane was subjected to a BatchMin multiple minimum search[11] using MM2 within MacroModel, the three lowest conformations were then converted back to the diphosphine and minimised using PM3; preferred conformations found this way seem reasonable (*e.g.* all cyclohexane rings are in chair form). It can be seen that the preference for the *cis*-structure decreases as the ring sizes get larger, but is still significant for **2e**, the only case where a mixture of isomers is formed. It seems likely that the transition states for formation of the *cis*- and *trans*-isomers will show similar con-

Table 1 Selected bond lengths (Å) and angles (°) for **2b.S$_2$** and **2c.S$_2$**

(a) **2b.S$_2$**	
P(1)–P(2)	2.208(3)
P(1)–S(1)	1.940(3)
P(1)–C(4)	1.807(8)
P(1)–C(7)	1.802(7)
P(2)–S(2)	1.940(3)
P(2)–C(1)	1.813(7)
P(2)–C(5)	1.811(7)
P(2)–P(1)–S(1)	113.3(1)
P(2)–P(1)–C(4)	106.9(3)
S(1)–P(1)–C(4)	114.5(3)
P(2)–P(1)–C(7)	93.3(3)
S(1)–P(1)–C(7)	116.1(3)
C(4)–P(1)–C(7)	110.7(3)
P(1)–P(2)–S(2)	115.9(1)
P(1)–P(2)–C(1)	103.6(3)
S(2)–P(2)–C(1)	114.9(3)
P(1)–P(2)–C(5)	93.7(3)
S(2)–P(2)–C(5)	118.5(3)
C(1)–P(2)–C(5)	107.4(4)
(b) **2c.S$_2$**	
P(1)–S(1)	1.945(1)
P(1)–C(4)	1.806(2)
P(1)–P(1A)	2.182(1)
P(1)–C(1A)	1.811(3)
S(1)–P(1)–C(4)	114.4(1)
S(1)–P(1)–P(1A)	113.8(1)
C(4)–P(1)–P(1A)	101.5(1)
S(1)–P(1)–C(1A)	115.7(1)
C(4)–P(1)–C(1A)	108.5(1)
P(1A)–P(1)–C(1A)	101.2(1)

Table 2 PM3 Calculated heats of formation for bicyclic [k.l.0]-diphosphines

Compound No.	Bicyclic[k.l.0]-diphosphine	*cis*/*trans*	ΔH_f (kJ mol^{-1})	$\Delta\Delta H_f$ (kJ mol^{-1})
2a		*cis*	−72.8	140.6
		trans	67.8	
2b		*cis*	−76.1	86.6
		trans	10.5	
2c		*cis*	−87.4	51.5
		trans	−35.9	
2d		*cis*	−98.3	77.8
		trans	−20.5	
2e		*cis*	−87.9	34.3
		trans	−53.6	
		*cis*	−76.1	14.6
		trans	−61.5	

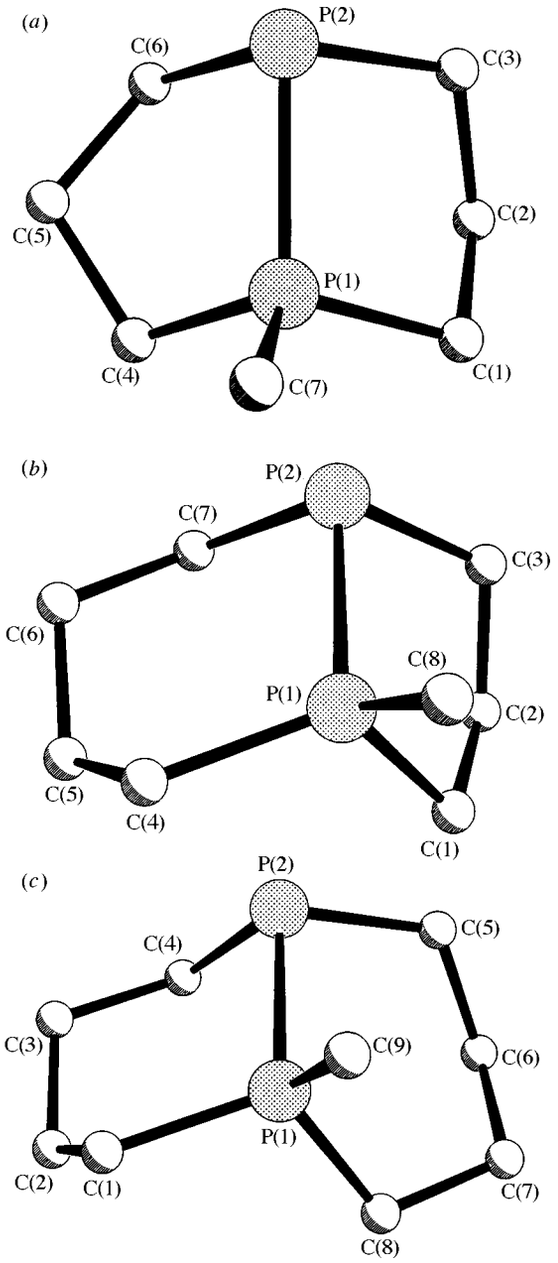


Fig. 2 X-Ray structure of the cations of (*a*) 1-methyl-1-phosphonia-5-phosphabicyclo[3.3.0]octane iodide **3a.I**, (*b*) 1-methyl-1-phosphonia-6-phosphabicyclo[4.3.0]nonane iodide **3b.I** and (*c*) 1-methyl-1-phosphonia-6-phosphabicyclo[4.4.0]decane iodide **3c.I**

figurational preferences to the final products, but with reduced energy differences due to the length of the forming P···C bond.

The bicyclic diphosphines **2** are readily quaternised by normal alkylating agents to give mono-quaternised salts **3a**–**e**; di-quaternisation only occurs with powerful reagents like methyl triflate (see later). In all cases the stereochemistry of the diphosphines **2** appears to be preserved in the salts **3**; X-ray structures for the iodide salts of **3a**–**c** are shown in Fig. 2, and selected bond lengths and angles for the three structures are given in Table 3. In these structures the P–P distances are close to 2.18 Å, with a marginal decrease accompanying the increased chain length from **3a** to **3b** to **3c**. The quaternary P–methyl distances are about 1.78 Å, rather smaller than the P–CH_2 distances which average 1.806 Å for the quaternary phosphorus P(1) and 1.859 Å for the tertiary phosphorus P(2). The effects of ring strain are most notable on the P–P–C angles of the 5-membered rings in **3a** and **3b** which are *ca.* 100° for the quaternary phosphorus and 89° for the tertiary phosphorus (*cf.* corresponding values of 109° and 96° for 6-membered rings), other angles at both P and C are closer to tetrahedral values.

In considering the reaction of alkyllithium or Grignard reagents with **3**, it is notable that attack occurs at the uncharged phosphorus atom. This reaction appears to be novel, although it has been shown that 1,2-diphenyl-1,2-diphospholane reacts

Table 3 Selected bond lengths (Å) and angles (°) for **3a.I** and **3b.I**

(a) **3a.I**	
P(1)–P(2)	2.183(2)
P(1)–C(1)	1.802(4)
P(1)–C(4)	1.811(5)
P(1)–C(7)	1.784(4)
P(2)–C(3)	1.863(4)
P(2)–C(6)	1.876(5)
P(2)–P(1)–C(1)	100.6(2)
P(2)–P(1)–C(4)	100.1(2)
C(1)–P(1)–C(4)	111.9(2)
P(2)–P(1)–C(7)	117.4(2)
C(1)–P(1)–C(7)	113.5(2)
C(4)–P(1)–C(7)	112.1(2)
P(1)–P(2)–C(3)	89.7(2)
P(1)–P(2)–C(6)	88.9(2)
C(3)–P(2)–C(6)	102.9(2)
(b) for **3b.I**	
P(1)–P(2)	2.179(3)
P(1)–C(1)	1.835(10)
P(1)–C(4)	1.801(8)
P(1)–C(8)	1.759(9)
P(2)–C(3)	1.849(9)
P(2)–C(7)	1.882(8)
P(2)–P(1)–C(1)	100.6(3)
P(2)–P(1)–C(4)	110.3(3)
C(1)–P(1)–C(4)	114.7(5)
P(2)–P(1)–C(8)	112.2(3)
C(1)–P(1)–C(8)	109.2(4)
C(4)–P(1)–C(8)	109.6(4)
P(1)–P(2)–C(3)	88.2(3)
P(1)–P(2)–C(7)	96.5(3)
C(3)–P(2)–C(7)	101.5(4)
(c) for **3c.I**	
P(1)–P(2)	2.173(2)
P(1)–C(1)	1.795(7)
P(1)–C(8)	1.805(7)
P(1)–C(9)	1.791(7)
P(2)–C(4)	1.855(7)
P(2)–C(5)	1.837(7)
P(3)–P(4)	2.171(2)
P(3)–C(14)	1.846(7)
P(3)–C(15)	1.861(8)
P(4)–C(11)	1.805(6)
P(4)–C(18)	1.802(8)
P(4)–C(19)	1.785(7)
P(2)–P(1)–C(1)	107.3(2)
P(2)–P(1)–C(8)	110.8(2)
C(1)–P(1)–C(8)	109.3(3)
P(2)–P(1)–C(9)	108.9(2)
C(1)–P(1)–C(9)	109.3(4)
C(8)–P(1)–C(9)	111.2(3)
P(1)–P(2)–C(4)	95.2(2)
P(1)–P(2)–C(5)	96.7(2)
C(4)–P(2)–C(5)	103.5(3)
P(4)–P(3)–C(14)	96.7(2)
P(4)–P(3)–C(15)	94.9(2)
C(14)–P(3)–C(15)	103.7(3)
P(3)–P(4)–C(11)	110.4(2)
P(3)–P(4)–C(18)	106.2(3)
C(11)–P(4)–C(18)	109.5(3)
P(3)–P(4)–C(19)	110.7(2)
C(11)–P(4)–C(19)	110.2(3)
C(18)–P(4)–C(19)	109.8(3)

with alkyllithium reagents with P–P bond cleavage,[12] and there are a number of examples of P–P bond cleavage resulting from addition of alkyl halides to tetraalkyldiphosphines.[13,14] The stereochemistry of the reaction at the $P–P^+$ bond of **3** can be accounted for by attack of the organometallic reagent along the P–P axis, accompanied by a least-motion ring opening process. It is possible that an intermediate like **A** is formed (see next page), although we have no evidence for or against this suggestion.

We now turn to the scope of the various steps in the formation of **3**. The 1,ω-diphosphinoalkanes **1a**–**c** were prepared by modification of the literature procedures for **1a**.[15,16] Handling procedures for these extremely noxious and pyrophoric compounds are detailed in the Experimental section. Procedures for the cyclisation of **1** were modelled on the method used by Issleib and Thorausch.[17] Thus a solution of the diphosphine **1a** in THF was treated with one equivalent of Bu^{n}Li at −78 °C and hydrogen was evolved from the reaction mixture on warming to room temperature. ^{31}P NMR spectra of reacting solutions clearly showed the presence of the acyclic mono-anion at −78 °C [δ_P −137.9 (t, $^1J_{PH}$ 190 Hz), −162.6 (d, $^1J_{PH}$ 155 Hz)], and this was replaced by signals for the cyclised mono-anion [δ_P −65.4 (dd, $^1J_{PP}$ 313, $^1J_{PH}$ 150 Hz), −141.9 (d)] as the solution was allowed to warm up, but the ^{31}P NMR spectra failed to reveal any intermediates in this remarkable reaction. After two hours the evolution of gas had subsided and a solution of the cyclic anion remained. From this point Issleib and Thorausch had used two procedures. The first was to treat a solution of the cyclic anion with a second equivalent of Bu^{n}Li to form the di-anion, which was then reacted with 1,3-dichloropropane to give **2a** in 11% yield. The second procedure involved the alkylation of the cyclic anion with 1-bromo-3-chloropropane, followed by cyclisation through addition of a second equivalent of Bu^{n}Li. Despite the extra manipulations that were involved, the latter procedure allowed the isolation of **2a** in an improved yield of 19%. The following further modifications to the second procedure doubled the original yield of **2a** to 40–45%:

i) The handling of air sensitive solutions was kept to a minimum (see the Experimental section).

ii) The first cyclisation stage was left for three hours instead of two.

iii) The solution of cyclic anion was added to the dihaloalkane over two hours. This ensured that the temperature remained at −78 °C.

iv) In the final intramolecular cyclisation the solvent was allowed to gently reflux as the Bu^{n}Li was added.

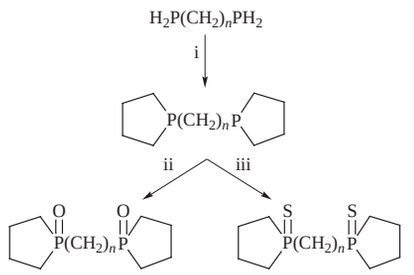
v) The phosphine was not separated from the inorganic salts prior to distillation.

Using this procedure, **2b** could be prepared in 31% yield from **1a**, but preparation by the alternative route from **1b** is slightly preferable (37% yield). Preparation of **2e** by this procedure gave only a 2% yield, but this could be increased to 11% by a five-fold decrease in the phosphine concentration. The low yield suggests that formation of seven-membered rings is close to the limit of this methodology.

Issleib and Thorausch had attempted the cyclisation of **1b** without success. We found however that this could be achieved by working in more dilute solution and leaving the cyclisation step to run for much longer (24 h). Using all the modifications described above, we were able to raise the yield of **2c** to 65%, and the mixture of isomers of **2e** could be obtained in 36% yield.

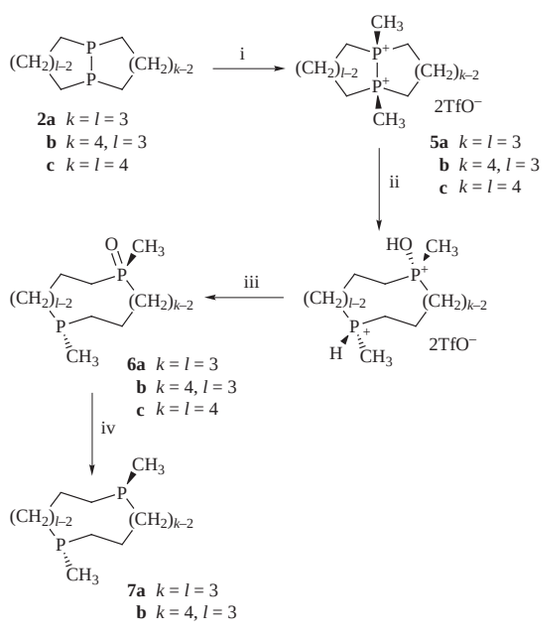
We tried to extend these procedures to the preparation of 1,7-diphosphabicyclo[5.5.0]dodecane starting from **1c**, but the cyclisation of the latter does not seem to compete with polymerisation. In dilute solution and after heating at 60 °C for 20 h, ^{31}P NMR suggested that at best only low concentrations of the cyclic mono-anion were present and attempts to trap this with 1-bromo-3-chloropropane to give **2d** were unsuccessful.

When 1,3-diphosphinopropane and 1,4-diphosphinobutane were treated with Bu^{n}Li at −78 °C, and then, without warming, with 1-bromo-4-chlorobutane, a second equivalent of Bu^{n}Li, and a second equivalent of 1-bromo-4-chlorobutane, followed by warming to 0 °C and the addition of two more equivalents of Bu^{n}Li, 1,3-(diphospholano)propane and 1,4-(diphospholano)butane were formed (Scheme 2). These compounds were useful for comparison purposes, but the yields were not optimised; they could be converted to dioxides and disulfides in the usual way (see the Experimental section).



Scheme 2 *Reagents and conditions*: i Bu^{n}Li, Br(CH$_2$)$_4$Cl, then Bu^{n}Li, −78–0 °C, 2 equiv. Bu^{n}Li; ii H_2O_2; iii S_8, PhH

The route to *trans*-1,*n*-disubstituted-1,*n*-diphosphacycloalkanes depends on dialkylation of 1,*k* + 2-diphosphabicyclo[*k*.*l*.0]alkanes **2** with powerful alkylating agents like methyl triflate, Scheme 3. The bicyclic di-cations **5** formed are hydrolysed instantly by water, and we were unable to obtain satisfactory analytical data for these salts. We have made tricyclic propellane analogues of these di-cations, some of which are much more stable hydrolytically, and our understanding of the stereoselectivity of the route to *trans*-1,*n*-disubstituted-1,*n*-diphosphacycloalkanes depends on analogies with the behaviour of these more stable analogues. The stereochemistry of the extremely rapid hydrolytic P–P cleavage of the bicyclic di-alkylated di-cations can be rationalised by attack of hydroxide along the P–P axis, accompanied by a least motion ring opening process. Although we have no direct evidence, it is possible that an intermediate like **B** is formed. In the case of tricyclic propellane dications which are hydrolysed much more slowly and in some cases reversibly, adducts which retain P–P bonding, *e.g.* **C**, can be isolated.[6] It is surprisingly easy to isolate the hydrolysis products as diprotonated di-cations, but these are readily converted to neutral diphosphine monooxides by treatment with

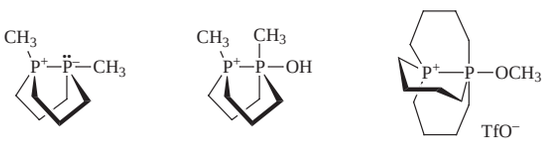


Scheme 3 *Reagents and conditions*: i MeOTf; ii H_2O; iii NaOH; iv $LiAlH_4$ in PhH

Table 4 NMR and photoelectron spectroscopic data for bicyclic[*k.l*.0]diphosphines

Compound	δ_P	N_{PC} (α-C)	N_{PC} (β-C)	N_{PC} (γ-C)	Ionisation energy, eV	CPC_{av} (°)[a]	CPX_{av} (°)[a]
2a	−27.81	31	9	—	8.6	102.7	97.5
2b	−56.95	25, 23	3, 4	—	8.3	102.1	101.0
2c	−77.47	20[a]	0[a]	—	8.2	98.3	101.2
2d	−49.36	31, 27	11, 23	11		101.5	102.9
cis-**2e**	−70.19	23, 15	6, 0	11		99.8	103.8
trans-**2e**	−48.34	8, 7	0, 0	10		108.2	103.0

[a] From PM3 calculations. CPC_{av} is the average of the C–P–C angles, and CPX_{av} is the average of all angles at phosphorus.



A **B** **C**

base. All these steps appear to be completely stereoselective (^{31}P NMR) but unfortunately we have not been able to find a reagent which will reduce the diphosphine monooxides completely stereoselectively to the *trans*-1,*n*-disubstituted-1,*n*-diphosphacycloalkanes. The best results were obtained with $LiAlH_4$ in benzene, which typically gave a 95 : 5 ratio of *trans*- to *cis*-isomer. Other reagents tried included $LiAlH_4$ in ether and THF, $HSiCl_3$ and Si_2Cl_6,[18–20] but these either failed to effect clean reduction or gave lower stereoselectivity. We also tried to develop an alternative route to these *trans*-isomers. Benzyl groups in phosphines like $PhCH_2PPhMe$ can be displaced with alkyllithium reagents with clean inversion of configuration.[21] However **4b** failed to react with either MeLi or Bu^{n}Li.

The properties of 1,*k* + 2-diphosphabicyclo[*k.l*.0]alkanes

NMR spectra. The ^{31}P chemical shifts (δ_P) observed in the 1,*k* + 2-diphosphabicyclo[*k.l*.0]alkanes vary widely with ring size (Table 4). Three principal factors are known to affect the ^{31}P chemical shift observed in compounds containing phosphorus.[22]

i) The bond angles at phosphorus and therefore the hybridisation.

ii) The amount of π-bonding between phosphorus and its substituents.

iii) The electronegativity of the substituents.

The phosphorus atoms in the series of bicyclic[*n.m*.0]diphosphines under investigation all have one phosphorus and two alkyl groups as their substituents. Therefore changes in δ_P can probably be attributed to changes in the bond angles at phosphorus, which will be significantly affected by the size of the rings in the bicyclic system. Table 4 also lists the bond angles at phosphorus calculated by PM3 for the range of diphosphines which have been synthesised. It is clear that as the CPC bond angle increases so does the ^{31}P chemical shift, although the trend with reference to the average of all the angles at phosphorus (CPX_{av}) is less clear. Of the two ^{31}P shifts for the isomers of **2e**, the value for the *cis*-isomer would be expected to be close to that for **2c**, as it has a similar average CPC bond angle; the two shifts have therefore been assigned on this basis.

The ^{13}C NMR spectra obtained for the bicyclic[*n.m*.0]diphosphines display either simple triplets or singlets for all the carbon resonances. For this reason, only N_{PC}, the sum of the two separate coupling constants (J_{PC} and $J_{P'C}$), can be measured and this yields no information about the absolute magnitudes of the PC couplings. The values of N_{PC} for the range of bicyclic[*n.m*.0]diphosphines are presented in Table 4.

Photoelectron spectra. The photoelectron spectra (PES) of **2a**–**c** were recorded (Fig. 3) for comparison with the PES of the corresponding hydrazines, which have been thoroughly studied.[23] In the hydrazine spectra, two ionisation bands were observed in the region corresponding to the loss of a lone pair electron, and a simple relationship between the degree of mixing and the lone pair torsion angle (θ) was observed. The band separation was greatest when θ was close to 0° and 180°, and

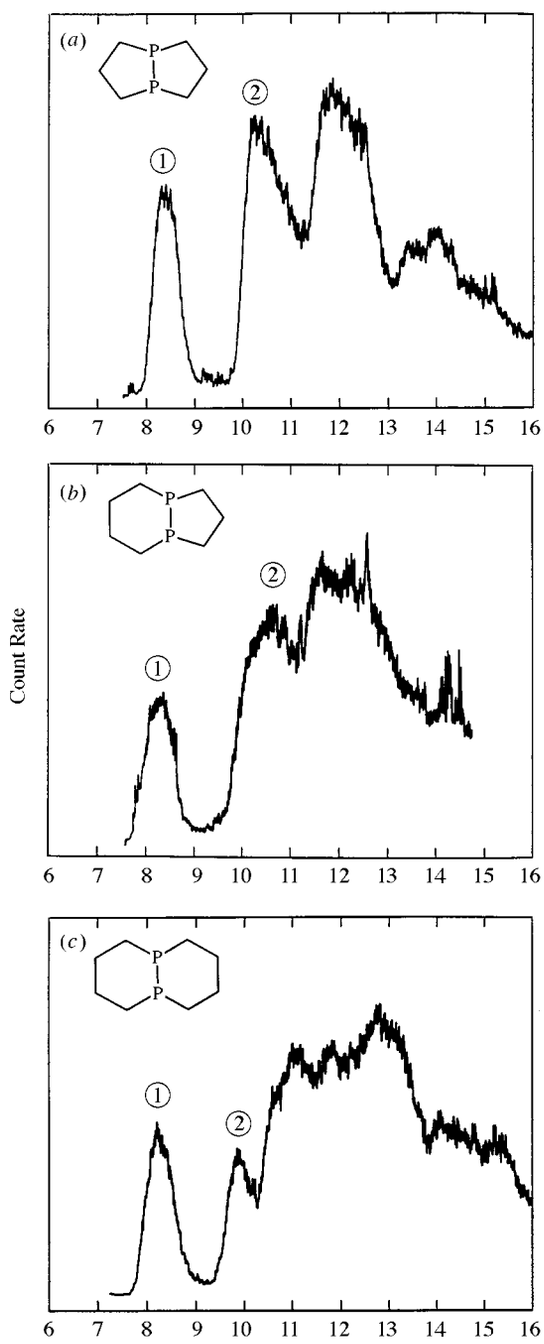


Fig. 3 He(I) photoelectron spectra of (*a*) 1,5-diphosphabicyclo[3.3.0]-octane **2a**, (*b*) 1,6-diphosphabicyclo[4.3.0]nonane **2b** and (*c*) 1,6-diphosphabicyclo[4.4.0]decane **2c**

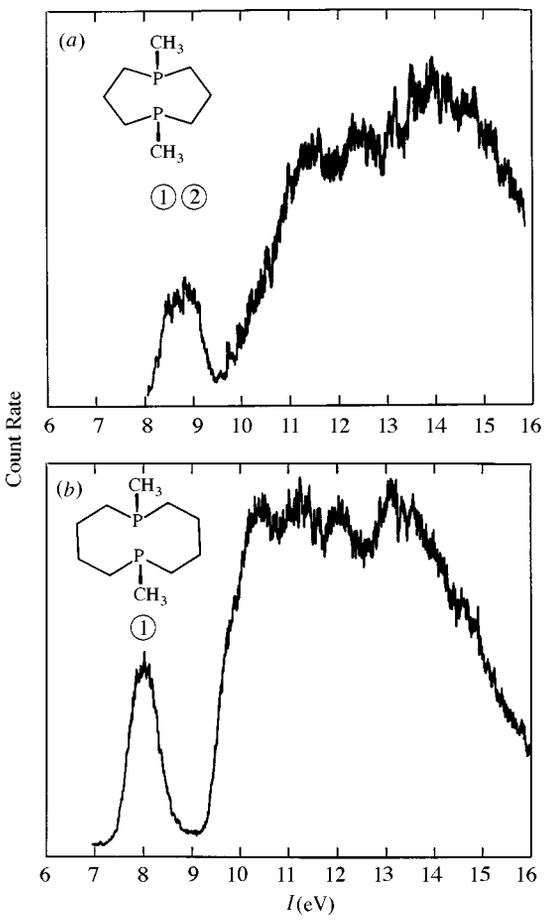


Fig. 4 He(I) photoelectron spectra of (*a*) 1,5-dimethyl-1,5-diphosphacyclooctane **4a** and (*b*) 1,6-dimethyl-1,6-diphosphacyclodecane **4f**

smallest when θ was close to 90°. In the diphosphines **2a**–**c** however, only one band was observed for the lone pair ionisations, which suggests insignificant mixing of the two lone pair orbitals. This probably reflects the greater s-orbital character and more localised nature of phosphorus lone pairs compared to those of nitrogen. Table 4 lists the lone pair ionisation energies that were obtained and the average bond angle (CPX_{av}) at phosphorus (from PM3 calculations). As the bond angles are increased the ionisation potential decreases. The flattening of the phosphorus nuclei will increase the p-orbital character of the lone pair, causing a decrease in the ionisation energy. Of course, ionisation energies tend to decrease as the carbon skeleton gets larger anyway.

The properties of *cis*-1,*n*-disubstituted-1,*n*-diphosphacycloalkanes

X-Ray crystal structural determinations for **4a** and **4f** have been published in our preliminary communication.[8] All attempts to induce crystallisation of *cis*-1,6-dimethyl-1,6-diphosphacyclononane **4e** failed, so the compound was converted to its disulfide by reaction with elemental sulfur in refluxing benzene and a crystal suitable for X-ray crystallography was grown by slow diffusion of diethyl ether into a saturated solution in dichloromethane. The X-ray data clearly showed that the disulfide adopts a *cis*-conformation, as expected, but was not of sufficient quality to obtain detailed structural information.

NMR Spectra. The ^{31}P NMR shifts for **4a**, **4e** and **4f** are −39.63, −39.77 and −37.32 respectively, and are all shifted upfield from related acyclic phosphines (*cf.* δ_P −34.0 for diethylmethylphosphine).[24] The upfield shifts can be attributed to a flattening of the phosphorus atoms, caused by the conformational constraints imposed by the medium-rings. Direct evidence for a significant transannular interaction in *cis*-1,5-dimethyl-1,5-diphosphacyclooctane **4a** comes from examination of its ^1H NMR spectrum. The methyl groups are virtual coupled triplets, suggesting a significant P···P coupling. The appearance of a triplet suggests that $J_{PP} \gg L_{PH}$ ($=J_{PH}-J_{P'H}$). This is confirmed by the spectra for the unsymmetrical systems **4b** and **4c**, where J_{PP} values are 36 and 56 Hz respectively. The ^{13}C NMR spectrum of **4a** is deceptively simple, with all the resonances appearing as simple triplets. In this case $J_{PP} \gg L_{PC}$ ($=J_{PC}-J_{P'C}$) and only N_{PC} can be measured (12 Hz for the α-carbons, significantly less than in the compounds containing a P–P bond). The ^{13}C NMR spectrum of the *trans*-isomer of **4a** suggests that in this case $J_{PP} \ll L_{PC}$ suggesting a much larger P···P distance. The ^{13}C NMR spectrum of 1,6-dimethyl-1,6-diphosphacyclononane **4e** displays 5- and 6-line signals for all but one of the carbon resonances, and a value of N_{PC} of about 10 Hz was obtained from simulation. The disulfide of **4e** shows only simple doublets and triplets, suggesting a further decrease in the P···P coupling compared with **4e**. The ^{13}C NMR of the ten-membered ring diphosphine **4f** is simple; all the α-carbons are doublets, and the β-carbons doublets of doublets. This suggests the P···P distance (4.97 Å) is too great for a significant through-space P···P coupling.

Photoelectron spectra. The PE spectrum of *cis*-1,5-dimethyl-1,5-diphosphaoctane **4a** shows two overlapping bands at 8.5 and 8.8 eV, while that of *cis*-1,6-dimethyl-1,6-diphosphadecane **4f** shows one band at 8.0 eV (see Fig. 4). We assign the band(s) below 9 eV to ionisation events from the lone pairs at phosphorus. This assignment is based on the comparison with the PE spectrum of trimethylphosphine which shows a similar first ionisation energy.[25] We ascribe the close proximity of the first two bands in the PE spectrum of **4a** and the coincidence in the case of **4f** to the high s character of the lone pair and a small spatial overlap between them. Unlike 1,5-diphosphabicyclo-[3.3.3]undecane, discussed in the accompanying paper,[26] there is no evidence of through-bond or through-space coupling in these cases.

Conclusions

We have described a stereoselective route to *cis*-1,*n*-disubstituted-1,*n*-diphosphacycloalkanes **4** which gives access to compounds with a variety of ring sizes. The route is flexible and should permit a range of substituents to be introduced on the phosphorus atoms. Although only compounds with simple $(CH_2)_n$ bridges between the phosphorus atoms have been made so far, incorporation of more elaborate bridges, including chiral structures should be possible. The structures of **4a** and **4f** show that the distance apart of the phosphorus atoms and the orientation of their lone pairs can be varied quite substantially. All this augurs well for the potential of these compounds as ligands, and we are currently examining the preparation of metal complexes of these diphosphines.

Experimental

General procedures

Solvents and reagents used in this work were purified according to standard literature techniques[27] and stored under nitrogen. Solvents were freshly distilled prior to use under an inert atmosphere and dispensed using gas tight syringes. Commercially available reagent solutions were used at the molarity stated and were regularly titrated. Due to the nature of this work, the majority of the reactions and work-ups were carried out under an oxygen- and moisture-free environment using Schlenk tube and related techniques. The highly pyrophoric primary phosphines required special attention and their manipulation was carried out in a fume hood fitted with a high grade filter specifically designed for the removal of arsines and related compounds. Melting points were obtained on a Reichert apparatus, using a thermocouple and a digital readout, and are

corrected. Elemental analyses were performed by the staff of the micro-analytical department of the School of Chemistry, University of Bristol. Electron Impact, Chemical Ionisation and Fast Atom Bombardment mass spectra were recorded by Dr K. MacNeil of the mass spectrometry service at the School of Chemistry, University of Bristol. The mass spectra of many of the phosphines contained peaks relating to the mono- and di-oxides—these are noted in the relevant section. NMR spectra were recorded on a JEOL GX400 machine which was operated at 399.8 MHz for ^{1}H spectra, 161.8 MHz for ^{31}P spectra and 100.5 MHz for ^{13}C spectra. The solvent used is stated in the relevant section. ^{1}H and ^{13}C spectra were referenced using either the residual non-deuterated solvent or tetramethylsilane, and ^{31}P spectra were externally referenced to 80% phosphoric acid. *J* Values are given in Hz.

1,*n* + 2-Diphosphabicyclo[*n.m.*0]alkanes and precursors

1,3-Bis(diethoxyphosphinyl)propane. Following the literature method,[28] 1,3-dibromopropane (80.8 g, 0.40 mol) and triethyl phosphite (166 g, 1.0 mol) were stirred and heated to 160–170 °C at atmospheric pressure. The reaction mixture was heated for approximately three hours during which time bromoethane distilled from the reaction vessel. The mixture was then allowed to cool and volatiles were removed *in vacuo*. The product was vacuum distilled (0.1 Torr, 160–162 °C, lit.,[28] 1 Torr, 178–180 °C) to give a colourless oil (88.6 g, 70%); $\delta_H(CDCl_3)$ 1.01 (12 H, t, $^{3}J_{HH}$ 7, CH_3), 1.64 (6 H, m), 3.77 (8 H, q, $^{3}J_{HH}$ 7, CH_2O); δ_C 15.55 (2 C, t, $^{2}J_{PC}$ 5, C-2), 15.78 (4 C, s, *C*H$_3$), 25.46 (2 C, dd, $^{1}J_{PC}$ 140, $^{3}J_{PC}$ 15, C-1, C-3), 60.85 (4 C, s, *C*H$_2$O); δ_P 30.20; *m/z* (EI) 316 (M$^+$, 0.25%), 179 {[M + 1]$^+$ − (EtO)$_2$P(O), 100}.

1,4-Bis(diethoxyphosphinyl)butane. The procedure above was employed, using 1,4-dibromobutane (86 g, 0.40 mol) and triethyl phosphite (156 g, 0.94 mol). The product was distilled (0.1 Torr, 178–180 °C, lit.,[28] 0.1 Torr, 171 °C) giving a colourless oil (98 g, 74%); $\delta_H(CDCl_3)$ 1.34 (12 H, t, $^{3}J_{HH}$ 7, CH_3), 1.73 (8 H, m), 3.78 (8 H, m, CH_2O); δ_C 15.84 (4 C, d, $^{3}J_{PC}$ 6, *C*H$_3$), 22.82 (2 C, dd, $^{2}J_{PC}$ 5, $^{3}J_{PC}$ 18, C-2, C-3), 24.64 (2 C, d, $^{1}J_{PC}$ 142, C-1, C-4), 60.72 (4 C, d, $^{2}J_{PC}$ 8, *C*H$_2$O); δ_P 31.14; *m/z* (CI) 331 ([M + 1]$^+$, 100%), 285 ([M + 1]$^+$ − EtOH, 16), 193 {[M + 1]$^+$ − (EtO)$_2$P(O)H, 14}.

1,5-Bis(diethoxyphosphinyl)pentane. The previous method was followed, using 1,5-dibromopentane (33.8 g, 0.15 mol) and triethyl phosphite (73.2 g, 0.44 mol). Distillation (0.1 Torr, 184–186 °C) yielded a colourless oil (39 g, 76%) [Found (EI): M$^+$, 344.1512. $C_{13}H_{30}O_6P_2$ requires 344.1518]; $\delta_H(CDCl_3)$ 1.32 (12 H, t, $^{3}J_{HH}$ 7, CH_3), 1.4–1.8 (10 H, m), 4.07 (8 H, m, CH_2O); δ_C 16.49 (4 C, d, $^{3}J_{PC}$ 6, *C*H$_3$), 22.05 (2 C, dd, $^{2}J_{PC}$ 5, $^{4}J_{PC}$ 1, C-2, C-4), 25.46 (2 C, d, $^{1}J_{PC}$ 141, C-1, C-5), 31.41 (1 C, t, $^{3}J_{PC}$ 16, C-3), 60.72 (4 C, d, $^{2}J_{PC}$ 6, *C*H$_2$O); δ_P 33.42; *m/z* (EI) 344 (M$^+$, 2%), 207 [M$^+$ − (EtO)$_2$P(O), 98], 193 [M$^+$ − (EtO)$_2$P(O)CH$_2$, 100].

1,3-Diphosphinopropane 1a. Following the literature procedure,[29] a solution of 1,3-bis(diethoxyphosphinyl)propane (129 g, 0.41 mol) in Et$_2$O (100 cm^3) was added dropwise to a suspension of LiAlH$_4$ (50 g, 1.32 mol) in Et$_2$O (1500 cm^3), cooled to 0 °C. After warming to room temperature the reaction was allowed to stir for three days. It was then cooled again in iced water and hydrolysed by careful addition of HCl (5 mol dm^{-3}, 600 cm^3). The clear ethereal layer was transferred by Teflon tubing to a flask containing anhydrous MgSO$_4$, to dry the organic phase. The aqueous phase was washed with Et$_2$O (100 cm^3) and this was combined with the rest of the ethereal layer. A portion of this solution was transferred into a 100 cm^3 flask set up for distillation. After removal of the bulk of the solvent a further portion of the solution was added. This procedure was repeated until all the solution had been transferred. The remaining solvent was removed and after a forerun of ethanol the product was distilled (760 Torr, 145–146 °C, lit.,[29] 725 Torr, 129–131 °C). This yielded a colourless, pyrophoric liquid with an obnoxious odour (27.4 g, 65%); $\delta_H(CDCl_3)$ 1.54 (4 H, br, 1-CH$_2$, 3-CH$_2$), 1.71 (2 H, br, 2-CH$_2$), 2.65 (4 H, d, $^{1}J_{PH}$ 194, PH_2); δ_C 13.30 (2 C, d, $^{1}J_{PC}$ 7, C-1, C-3), 33.65 (1 C, s, C-2); δ_P −138.48 (t, $^{1}J_{PH}$ 194). During the distillation care was taken to prevent leakage through any of the joints, as this leads to spontaneous combustion of the product. Due to the nature of the product, all glassware was soaked in aqueous sodium hypochlorite for at least a week before removal from the fume hood.

1,4-Diphosphinobutane 1b. A solution of 1,4-bis(diethoxyphosphinyl)butane (98 g, 0.30 mol) in Et$_2$O (100 cm^3) was added to a suspension of LiAlH$_4$ (36 g, 0.95 mol) stirred in Et$_2$O (1000 cm^3) at 0 °C. The procedure and work-up were as for the previous reaction. Distillation (760 Torr, 170–172 °C, lit.,[29] 13 mbar, 64.5 °C) gave a clear foul-smelling, pyrophoric liquid (11.6 g, 62%); $\delta_H(CDCl_3)$ 1.49 (4 H, m, 1-CH$_2$, 4-CH$_2$), 1.55 (4 H, m, 2-CH$_2$, 3-CH$_2$), 2.66 (4 H, d, $^{1}J_{PH}$ 195, PH_2); δ_C 13.31 (2 C, d, $^{1}J_{PC}$ 8, C-1, C-4), 33.66 (2 C, s, C-2, C-3); δ_P −137.48 (t, $^{1}J_{PH}$ 195).

1,5-Diphosphinopentane 1c. A solution of 1,5-bis(diethoxyphosphinyl)pentane (39 g, 0.11 mol) in Et$_2$O (50 cm^3) was added to a suspension of LiAlH$_4$ (15 g, 0.39 mol) stirred in Et$_2$O (450 cm^3) at 0 °C. The procedure and work-up were as previously described. Distillation (760 Torr, 190–192 °C) gave a clear pyrophoric liquid with an obnoxious odour (8.3 g, 55%); $\delta_H(CDCl_3)$ 1.51 (10 H, m), 2.69 (4 H, d, $^{1}J_{PH}$ 192, PH_2); δ_C 13.68 (2 C, d, $^{1}J_{PC}$ 9, C-1, C-5), 32.42 (1 C, s, C-3), 32.58 (2 C, s, C-2, C-4); δ_P −137.25 (t, $^{1}J_{PH}$ 192). Due to the unpleasant nature of this compound further analysis was not performed.

***cis*-1,5-Diphosphabicyclo[3.3.0]octane 2a.** Based on the literature method,[17] a solution of 1,3-diphosphinopropane (6.9 g, 64 mmol) in THF (70 cm^3), cooled to −78 °C, was treated with a solution of *n*-butyllithium in hexanes (2.5 mol dm^{-3}, 25.5 cm^3, 64 mmol). The reaction mixture was slowly warmed to room temperature, during which time it began to evolve hydrogen. After four hours of stirring at room temperature a golden solution remained. This was slowly transferred, over two hours, through narrow bore Teflon tubing, to a flask containing a stirred solution of 1-bromo-3-chloropropane (10.1 g, 64 mmol) in Et$_2$O (100 cm^3), cooled to −78 °C. After warming to room temperature the resulting colourless solution was treated with a solution of *n*-butyllithium in hexanes (2.5 mol dm^{-3}, 25.5 cm^3, 64 mmol) which caused gentle refluxing of the solvent. When the addition was complete all volatiles were removed by distillation (760 Torr) to leave a white solid residue. The product was distilled from this residue under high vacuum (0.1 Torr, 66–68 °C, lit.,[17] 0.1 Torr, 60–63 °C) to give a clear liquid (3.8 g, 40%); $\delta_H(CDCl_3)$ 1.4–1.7 (10 H, m), 1.91 (2 H, m); δ_C 30.81 (4 C, t, N_{PC} 9, C-2, C-4, C-6, C-8), 31.15 (2 C, t, $^{2}J_{PC}$ 15, C-3, C-7); δ_P −27.81. Addition of one equivalent of triflic acid to a CD_2Cl_2 solution of **2a** gave a solution containing 1-phosphonia-5-phosphabicyclo[3.3.0]octane trifluoromethanesulfonate, with slow proton exchange between the phsophorus atoms: $\delta_P(CD_2Cl_2$, −70 °C) 47.08 (dd, $^{1}J_{PP}$ 241, $^{1}J_{PH}$ 539, P-1), −53.90 (d, $^{1}J_{PP}$ 241, P-6).

***cis*-1,6-Diphosphabicyclo[4.3.0]nonane 2b.** A stirred solution of 1,4-diphosphinobutane (5.1 g, 42 mmol) in THF (220 cm^3), cooled to −78 °C was treated with a solution of *n*-butyllithium in hexanes (2.5 mol dm^{-3}, 17 cm^3, 42 mmol). The reaction mixture was slowly warmed to room temperature, during which time gas began to evolve. After two hours of stirring at room temperature a golden solution remained. This was slowly transferred, over two hours, through narrow bore Teflon tubing to a flask containing 1-bromo-3-chloropropane (6.6 g, 42 mmol) in Et$_2$O (50 cm^3), cooled to −78 °C. After warming to room temperature the resulting clear colourless solution was treated with a solution of *n*-butyllithium in hexanes (2.5 mol dm^{-3}, 17 cm^3, 42 mmol). The work-up was as described for the previous reaction, vacuum distillation (0.1 Torr, 80–85 °C) gave a clear liquid (2.4 g, 36%) [Found (EI): M$^+$, 160.0581. $C_7H_{14}P_2$ requires 160.0571]; $\delta_H(CDCl_3)$ 1.4–2.2 (14 H, m); δ_C 19.58 (2 C, t, N_{PC}

25, C-2, C-5), 21.92 (2 C, t, N_{PC} 4, C-3, C-4), 26.48 (2 C, t, N_{PC} 23, C-7, C-9), 27.28 (1 C, t, $^2J_{PC}$ 3, C-8); δ_P −56.95. Addition of one equivalent of triflic acid to a CD_2Cl_2 solution of **2b** gave a solution containing 1-phosphonia-6-phosphabicyclo[4.3.0]-nonane trifluoromethanesulfonate, with slow proton exchange between the phosphorus atoms: δ_P(CD_2Cl_2, −70 °C) 4.05 (dd, $^1J_{PP}$ 257, $^1J_{PH}$ 505, P-1), −73.04 (d, $^1J_{PP}$ 257, P-6).

***cis*-1,6-Diphosphabicyclo[4.3.0]nonane-1,6-disulfide.** 1,6-Diphosphabicyclo[4.3.0]nonane (32 mg, 0.20 mmol) in benzene (1 cm^3) was treated with sulfur (30 mg, 0.12 mmol) and heated at reflux for one hour. The solvent was removed *in vacuo* to leave a yellow residue which was extracted with CH_3CN (2 × 2 cm^3) and filtered to remove the excess sulfur. The solvent was removed to leave an off-white solid, in quantitative yield, which was recrystallised from acetonitrile and Et_2O mp 140–145 °C (Found: C, 37.6; H, 6.6. $C_7H_{14}P_2S_2$ requires C, 37.5; H, 6.3%); δ_H(CD_3CN) 1.7–2.5 (14 H, m); δ_C 20.51 (1 C, s, C-6), 22.31 (2 C, s, C-2, C-3), 33.89 (2 C, t, N_{PC} 44, C-1, C-4), 34.11 (2 C, t, N_{PC} 59, C-5, C-7); δ_P 37.20; *m*/*z* (EI) 224 (M^+, 100%), 160 (30). Diffusion tank recrystallisation, from acetonitrile and Et_2O, gave colourless crystals suitable for X-ray analysis.

***cis*-1,6-Diphosphabicyclo[4.4.0]decane 2c.** A stirred solution of 1,4-diphosphinobutane (4.7 g, 39 mmol) in THF (200 cm^3) at −78 °C was treated with a solution of *n*-butyllithium in hexanes (2.5 mol dm^{-3}, 15.5 cm^3, 39 mmol). The solution was warmed to room temperature and stirred for 24 hours. The resulting pale yellow solution, which contained a fine white precipitate, was then slowly transferred, over two hours, through Teflon tubing into a flask containing 1-bromo-4-chlorobutane (6.6 g, 39 mmol) in Et_2O (80 cm^3) cooled to −78 °C. After warming to room temperature a clear solution remained. This was treated with a solution of *n*-butyllithium in hexanes (2.5 mol dm^{-3}, 15.5 cm^3, 39 mmol) to leave a clear solution with an insoluble white precipitate. The bulk of the solvent was then removed by distillation (760 Torr) and the remainder under high vacuum to leave a white solid residue. A sublimation apparatus, fitted with a male joint, was inserted into the flask and the product was sublimed (1 Torr, 150 °C, two hours). This furnished a waxy white solid (4.4 g, 65%) mp 43–45 °C (Found: C, 55.0; H, 9.35. $C_8H_{16}P_2$ requires C, 55.2; H, 9.3%); δ_H($CDCl_3$) 1.64 (8 H, m), 1.85 (4 H, m), 2.09 (4 H, m); δ_C 18.32 (4 C, br, C-2, C-5, C-7, C-10), 23.11 (4 C, br, C-3, C-4, C-8, C-9); δ_C($[^2H_8]$toluene, 90 °C) 19.52 (4 C, t, N_{PC} 19, C-2, C-5, C-7, C-10), 24.48 (4 C, br, C-3, C-4, C-8, C-9); δ_C(CD_2Cl_2, −80 °C) 13.56 (2 C, t, N_{PC} 19, axial-CH_2P), 20.07 (2 C, s), 20.46 (2 C, t, N_{PC} 14, equatorial-CH_2P), 24.44 (2 C); δ_P −77.47; *m*/*z* (EI) 174 (M^+, 55%), 120 (44). A small sample of the title compound was sealed in an evacuated Schlenk tube, the end of which was immersed in an oil bath maintained at 40 °C. The diphosphine slowly sublimed to the top of the tube to give colourless crystals, which were suitable for X-ray structural analysis. Addition of one equivalent of triflic acid to a CD_2Cl_2 solution of **2c** gave a solution containing 1-phosphonia-6-phosphabicyclo[4.3.0]nonane trifluoromethanesulfonate, with slow proton exchange between the phsophorus atoms: δ_P(CD_2Cl_2, −60 °C) −29.07 (dd, $^1J_{PP}$ 253, $^1J_{PH}$ 491, P-1), −85.13 (d, $^1J_{PP}$ 253, P-6).

***cis*-1,6-Diphosphabicyclo[4.4.0]decane-1,6-disulfide.** Using a similar procedure to that described above, reaction of a solution of 1,6-diphosphabicyclo[4.4.0]decane (80 mg, 0.34 mmol) in benzene with sulfur (62 mg, 0.24 mmol) gave a white solid mp 150–155 °C (Found: C, 40.5; H, 7.0. $C_8H_{16}P_2S_2$ requires C, 40.3; H, 6.8%); δ_H(CD_2Cl_2) 1.85 (4 H, m), 2.0–2.4 (12 H, m); δ_C 22.38 (4 C, C-2, C-3, C-6, C-7), 30.37 (4 C, t, N_{PC} 42, C-1, C-4, C-5, C-8); δ_C(CD_2Cl_2, −85 °C) 19.17 (2 C), 23.20 (2 C), 26.97 (2 C, t, N_{PC} 39), 30.17 (2 C, t, N_{PC} 44); δ_P 28.78; *m*/*z* (EI) 238 (M^+, 100%), 205 (74), 173 (15). Diffusion tank recrystallisation, from acetonitrile and Et_2O, gave colourless crystals suitable for X-ray analysis.

***cis*-1,7-Diphosphabicyclo[5.3.0]decane 2d.** A solution of 1,3-diphosphinopropane (1.45 g, 13.4 mmol) in THF (20 cm^3) was cooled to −78 °C and treated with a solution of *n*-butyllithium in hexanes (2.5 mol dm^{-3}, 5.4 cm^3, 13.4 mmol). After warming to room temperature the reaction was left to stir for four hours. The resulting yellow solution was transferred, over two hours, through narrow bore Teflon tubing into a flask containing a solution of 1-bromo-5-chloropentane (2.49 g, 13.4 mmol) in Et_2O (150 cm^3) maintained at −78 °C. After warming to room temperature the resulting clear solution was treated with a solution of *n*-butyllithium in hexanes (2.5 mol dm^{-3}, 5.4 cm^3, 13.4 mmol) to give a colourless solution containing a white precipitate. After removal of the volatiles *in vacuo* the product was distilled (0.1 Torr, 78–81 °C) from the solid residue to yield a clear oil (0.25 g, 11%) [Found (CI): M^+, 174.0719. $C_8H_{16}P_2$ requires 174.0727]; δ_H($CDCl_3$) 1.3–2.0 (16 H, m); δ_C 22.31 (2 C, t, N_{PC} 31, C-2, C-6), 26.03 (1 C, t, $^2J_{PC}$ 5, C-4), 27.68 (1 C, t, $^2J_{PC}$ 11, C-9), 29.12 (2 C, t, N_{PC} 23, C-3, C-5), 29.32 (2 C, t, N_{PC} 27, C-8, C10); δ_P −49.36; *m*/*z* (CI) 175 ($[M + 1]^+$, 25%), 191 ($[M + 1]^+ + O$, 74), 207 ($[M + 1]^+ + O_2$, 100).

1,7-Diphosphabicyclo[5.4.0]undecane 2e. A stirred solution of 1,4-diphosphinobutane (198 mg, 1.62 mmol) in THF (10 cm^3) at −78 °C was treated with a solution of *n*-butyllithium in hexanes (2.5 mol dm^{-3}, 0.65 cm^3, 1.62 mmol). After warming to room temperature the reaction was left for two hours, and then slowly transferred through Teflon tubing, over two hours, into a flask containing 1-bromo-5-chloropentane (301 mg, 1.62 mmol) in Et_2O (10 cm^3), cooled to −78 °C. The reaction was warmed to room temperature, and treated with *n*-butyllithium in hexanes (2.5 mol dm^{-3}, 0.65 cm^3, 1.62 mmol) to leave a clear solution with a white precipitate. All volatiles were removed under high vacuum to leave a white solid. The title compound was obtained, as a clear oil, by Kügelrohr distillation (0.1 Torr, 130 °C), and was obtained as a mixture of *cis*- and *trans*-isomers (111 mg, 36%) [Found (CI): M^+, 188.0879. $C_9H_{18}P_2$ requires 188.0884]; δ_H($CDCl_3$) 1.2–2.3 (m); δ_C(*cis*-isomer) 19.53 (2 C, t, N_{PC} 15), 22.44 (2 C, t, N_{PC} 23), 23.19 (2 C, s), 23.54 (2 C, t, N_{PC} 6), 28.84 (1 C, t, $^3J_{PC}$ 5, C-4), (*trans*-isomer) 24.72 (2 C, t, N_{PC} 8), 26.35 (1 C, t, $^3J_{PC}$ 3, C-3), 26.82 (2 C, s), 27.58 (2 C, t, N_{PC} 10), 27.77 (2 C, s); δ_P −70.19 (*cis*-isomer, 75%), −48.34 (*trans*-isomer, 25%); *m*/*z* (CI) 189 ($[M + 1]^+$, 80%), 205 ($[M + 1]^+ + O$, 25), 221 ($[M + 1]^+ + O_2$, 32). This mixture of phosphines was analysed by GCMS on a Fison MD800 instrument fitted with a SGE BPXS column. The starting temperature was 70 °C which was ramped at 15 °C min^{-1} to a final temperature of 220 °C.

1,3-Bis(1-phospholano)propane. A solution of *n*-butyllithium in hexanes (2.1 mol dm^{-3}, 10.1 cm^3, 21.3 mmol) was added to a solution of 1,3-diphosphinopropane (2.3 g, 21 mmol) in THF (100 cm^3), at −78 °C, and the reaction stirred at this temperature for a further five minutes. To this mixture, maintained at −78 °C, was added 1-bromo-4-chlorobutane (3.65 g, 21.3 mmol) dissolved in Et_2O (10 cm^3). After another five minutes, a second equivalent of *n*-butyllithium in hexanes was added (2.1 mol dm^{-3}, 10.1 cm^3, 21.3 mmol) followed, after five minutes, by a second portion of 1-bromo-4-chlorobutane (3.65 g) in Et_2O. The reaction flask was warmed to 0 °C and a further two equivalents of *n*-butyllithium in hexanes (2.1 mol dm^{-3}, 20.2 cm^3, 42.6 mmol) was added dropwise, over five minutes. After stirring at room temperature for a further 30 minutes, solvent and volatiles were removed *in vacuo* (0.1 Torr), and the residue extracted (2 × 20 cm^3 Et_2O) and filtered through a glass sinter. Et_2O was removed *in vacuo*, and the residue vacuum distilled (0.1 Torr, 115–120 °C) to yield a pale yellow oil (0.54 g, 12%) [Found (EI): M^+, 216.1191. $C_{11}H_{22}P_2$ requires 216.1197]; δ_H($CDCl_3$) 1.2–1.8 (22 H, m); δ_C 24.42 (1 C, t, $^2J_{PC}$ 16, C-2), 26.02 (4 C, d, $^1J_{PC}$ 12, phospholano-CH_2P), 27.91 (4 C, d, $^2J_{PC}$ 3, phospholano-CH_2CH_2P), 30.78 (2 C, dd, $^1J_{PC}$ 16, $^3J_{PC}$ 11, C-1, C-3); δ_P −27.48; *m*/*z* (CI) 216, (M^+, 60%), 160 (100), 129 (73).

1,3-Bis(1-phospholano)propane-1,3-disulfide. Using a similar procedure to that described above, reaction of a solution of 1,3-bis(1-phospholano)propane (126 mg, 0.45 mmol) in benzene

with sulfur (57 mg, 0.22 mmol) gave a white solid which was recrystallised from CH_2Cl_2 and Et_2O mp 110–112 °C [Found (EI): M^+, 294.0808. $C_{12}H_{24}P_2S_2$ requires 294.0795; measured, $C_{11}H_{22}P_2S_2$ requires C, 47.1; H, 7.9%]; $\delta_H(CD_2Cl_2)$ 1.3–2.2 (22 H, m); δ_C 17.48 (1 C, t, $^2J_{PC}$ 2, C-2), 25.94 (4 C, d, $^2J_{PC}$ 6, phospholano-CH_2CH_2P), 33.52 (4 C, d, $^1J_{PC}$ 52, phospholano-CH_2P), 33.65 (2 C, dd, $^1J_{PC}$ 45, $^3J_{PC}$ 12, C-1, C-3); δ_P 62.96; *m*/*z* (EI) 280 (M^+, 81.3%), 161 (100), 119 (95).

1,3-Bis(1-phospholano)propane-1,3-dioxide. 1,3-Bis(1-phospholano)propane (50 mg, 0.23 mmol) dissolved in acetonitrile (1 cm^3) was treated with an aqueous solution of H_2O_2 (35%, 0.2 cm^{-3}) and stirred at room temperature for one hour. Solvent and volatiles were removed *in vacuo* to leave an oily residue. Attempts to recrystallise the residue (CH_3CN–Et_2O) were unsuccessful [Found (EI): M^+, 248.1111. $C_{11}H_{22}O_2P_2$ requires 248.1095]; $\delta_H(CD_3CN)$ 1.4–2.0 (22 H, m); δ_C 16.12 (1 C, d, $^1J_{PC}$ 3, C-2), 25.02 (4 C, d, $^2J_{PC}$ 8, phospholano-CH_2CH_2P), 27.17 (4 C, d, $^1J_{PC}$ 65, phospholano-CH_2P), 31.39 (2 C, dd, $^1J_{PC}$ 61, $^3J_{PC}$ 12, C-1, C-3); δ_P 75.92; *m*/*z* (EI) 248 (M^+, 7%), 145 (37), 131 (100), 118 (42).

1,4-Bis(1-phospholano)butane. Following the procedure and work-up described for preparing 1,3-bis(1-phospholano)-propane, a stirred solution of 1,4-diphosphinobutane (1.09 g, 8.9 mmol) in THF (50 cm^3) was treated twice, sequentially, with *n*-butyllithium in hexanes (2.2 mol dm^{-3}, 4.05 cm^3, 8.9 mmol) then 1-bromo-4-chlorobutane (1.53 g, 8.9 mmol) in Et_2O (10 cm^3) at −78 °C. Double cyclisation was effected on addition of a further two equivalents of *n*-butyllithium in hexanes (2.2 mol dm^{-3}, 8.1 cm^3, 18 mmol) at 0 °C. Vacuum distillation of the residue (0.1 Torr, 110–115 °C) gave an oil (0.57 g, 28%), which solidified on standing at room temperature to give a waxy solid mp 29–30 °C [Found (EI): M^+, 230.1365. $C_{12}H_{24}P_2$ requires 230.1353]; $\delta_H(C_6D_6)$ 1.21 (4 H, m), 1.39 (4 H, m), 1.5–1.7 (8 H, m); δ_C 24.92 (4 C, d, $^1J_{PC}$ 12, phospholano-CH_2P), 26.76 (4 C, d, $^2J_{PC}$ 4, phospholano-CH_2CH_2P), 27.46 (2 C, X part of an AA′X system, N_{PC} 29, C-2, C-3), 27.70 (2 C, d, $^1J_{PC}$ 16, C-1, C-4); δ_P −26.51; *m*/*z* (EI) 230 (M^+, 33%), 201 (26), 174 (86), 143 (100).

1,4-Bis(1-phospholano)butane-1,4-disulfide. Using a similar procedure to that described above, reaction of a solution of 1,4-bis(1-phospholano)butane (130 mg, 0.44 mmol) in benzene with sulfur (60 mg, 0.23 mmol) gave a white solid which was recrystallised from CH_2Cl_2 and Et_2O mp 115–118 °C [Found (EI): M^+, 294.0808. $C_{12}H_{24}P_2S_2$ requires 294.0795]; $\delta_H(CD_2Cl_2)$ 1.7–2.1 (24 H, m); δ_C 24.20 (2 C, dd, $^2J_{PC}$ 3, $^3J_{PC}$ 15, C-2, C-3), 26.07 (4 C, d, $^2J_{PC}$ 6, phospholano-CH_2CH_2P), 33.29 (2 C, d, $^1J_{PC}$ 45, C-1, C-4), 33.46 (4 C, d, $^1J_{PC}$ 52, phospholano-CH_2P); δ_P 63.28; *m*/*z* (EI) 294 (M^+, 44%), 175 (100).

1,4-Bis(1-phospholano)butane-1,4-dioxide. To a stirred solution of 1,4-bis(1-phospholano)butane (55 mg, 0.24 mmol) in CH_2Cl_2 (3 cm^3) at 0 °C was added an aqueous solution of H_2O_2 (35%, 0.2 cm^3). The mixture was stirred at room temperature for one hour, then the solvent and volatiles were removed *in vacuo* to leave an oily residue (0.071 g) which solidified on standing. This was recrystallised from acetonitrile and Et_2O to give colourless crystals, mp 115–120 °C [Found (EI): M^+, 262.1228. $C_{12}H_{24}O_2P_2$ requires 262.1251]; $\delta_H(CD_3CN)$ 1.4–2.1 (24 H, m); δ_C 24.01 (2 C, dd, $^2J_{PC}$ 4, $^3J_{PC}$ 13, C-2, C-3), 25.08 (4 C, d, $^2J_{PC}$ 7, phospholano-CH_2CH_2P), 27.32 (4 C, d, $^1J_{PC}$ 65, phospholano-CH_2P), 30.25 (2 C, d, $^1J_{PC}$ 62, C-1, C-4); δ_P 74.74; *m*/*z* (EI) 262 (M^+, 2.5%), 233 (11), 206 (11.1), 159 (100).

Monoalkylated 1,*k* + 2-diphosphabicyclo[*k*.*l*.0]alkanes

1-Methyl-1-phosphonia-5-phosphabicyclo[3.3.0]octane iodide 3a.I. In accordance with the literature method,[17] a solution of 1,5-diphosphabicyclo[3.3.0]octane (458 mg, 3.14 mmol) in Et_2O (20 cm^3) was treated with a two-fold excess of methyl iodide (0.39 cm^3, 6.3 mmol). The reaction mixture was stirred for 20 hours, during which time a thick white precipitate formed. All volatiles were removed *in vacuo* to leave a white crystalline solid in quantitative yield which was used without further purification, mp >300 °C; $\delta_H(CD_3OD)$ 2.0–2.5 (10 H, m), 2.16 (3 H, dd, $^2J_{PH}$ 15, $^3J_{PH}$ 4, CH_3), 2.5–2.6 (2 H, m); δ_C 6.15 (1 C, dd, $^1J_{PC}$ 44.2, $^2J_{PC}$ 13, CH_3), 27.76–28.10 (4 C, 7 signals, complex multiplet), 28.80 (2 C, dd, $^1J_{PC}$ 27.5, $^2J_{PC}$ 6, C-1, C-6); δ_P −52.32 (d, $^1J_{PP}$ 242, P-5), 77.09 (d, $^1J_{PP}$ 242, P-1); *m*/*z* (FAB^+) 161 (M^+ − I, 100%). Diffusion tank recrystallisation, using a solution of the iodide salt in methanol, with slow diffusion of Et_2O into the inner tank, gave colourless crystals of sufficient quality for X-ray structural analysis.

1-Methyl-1-phosphonia-5-phosphabicyclo[3.3.0]octane trifluoromethanesulfonate 3a.OTf. 1,5-Diphosphabicyclo[3.3.0]-octane (466 mg, 3.19 mmol) in CH_2Cl_2 (20 cm^3) was treated with methyl trifluoromethanesulfonate (0.36 cm^3, 3.2 mmol). After stirring for one hour a clear solution remained from which all volatiles were removed *in vacuo* to leave a white solid residue. After washing with Et_2O (2 × 20 cm^3) the solid was dried under high vacuum to give the title compound as a white powder (960 mg, 97%). The spectroscopic data is essentially identical to that of 1-methyl-1-phosphonia-5-phosphabicyclo-[3.3.0]octane iodide.

1-Methyl-1-phosphonia-6-phosphabicyclo[4.3.0]nonane iodide 3b.I. 1,6-Diphosphabicyclo[4.3.0]nonane (270 mg, 1.69 mmol) in Et_2O (10 cm^3) was treated with a twofold excess of methyl iodide (0.22 cm^3, 3.4 mmol). After stirring overnight a thick white precipitate had formed. Removal of all volatiles *in vacuo* furnished the title compound as a white solid in quantitative yield, mp >300 °C (Found: C, 31.6; H, 5.9. $C_8H_{17}IP_2$ requires C, 31.8; H, 5.7%); $\delta_H(CD_3OD)$ 1.4–1.8 (4 H, m), 1.87 (3 H, dd, $^2J_{PH}$ 14, $^3J_{PH}$ 6, CH_3), 1.9–2.5 (8 H, m), 2.6–2.7 (2 H, m); δ_P −66.02 (d, $^1J_{PP}$ 248, P-6), 35.25 (d, $^1J_{PP}$ 248, P-1); *m*/*z* (FAB^+) 175 (M^+ − I, 100%). Diffusion tank recrystallisation using methanol and Et_2O gave colourless crystals which were subjected to an X-ray structural analysis.

1-Methyl-1-phosphonia-6-phosphabicyclo[4.4.0]decane iodide 3c.I. Following the literature procedure,[9] 1,6-diphosphabicyclo-[4.4.0]decane (312 mg, 1.79 mmol) in Et_2O (10 cm^3) was treated with two equivalents of methyl iodide (0.23 cm^3, 3.6 mmol). The general procedure was as for the previous reaction and furnished a white solid in quantitative yield, mp >300 °C (Found: C, 34.2; H, 6.4. $C_9H_9IP_2$ requires C, 34.2; H, 6.1%); $\delta_H(CD_3OD)$ 1.6–1.8 (2 H, m), 1.8–2.1 (8 H, m), 1.94 (3 H, dd, $^2J_{PH}$ 14, $^3J_{PH}$ 6, CH_3), 2.1–2.3 (4 H, m), 2.5–2.7 (2 H, m); δ_C 6.81 (1 C, dd, $^1J_{PC}$ 46, $^2J_{PC}$ 12, CH_3), 17.65 (2 C, d, $^1J_{PC}$ 19, C-4, C-5), 18.80 (2 C, d, $^1J_{PC}$ 36, C-1, C-8), 21.49 (2 C, d, $^2J_{PC}$ 7, C-2, C-7), 21.73 (2 C, d, $^2J_{PC}$ 4, C-3, C-6); δ_P −74.57 (d, $^1J_{PP}$ 246, P-6), −3.55 (d, $^1J_{PP}$ 246, P-1); *m*/*z* (FAB^+) 189 (M^+ − I, 100%). Diffusion tank recrystallisation using methanol and Et_2O gave crystals suitable for an X-ray structural analysis.

1-Benzyl-1-phosphonia-5-phosphabicyclo[3.3.0]octane bromide 3d.Br. Benzyl bromide (4.1 cm^3, 34 mmol) was added to a solution of 1,5-diphosphabicyclo[3.3.0]octane (2.52 g, 17.1 mmol) in Et_2O (50 cm^3). After stirring for 20 hours the white precipitate which had formed was filtered off, and washed with Et_2O (3 × 50 cm^3). The product was obtained as a white solid (5.06 g, 94%) mp 153–155 °C; $\delta_H(CD_2Cl_2)$ 1.9–2.3 (8 H, m), 2.4–2.7 (4 H, m), 4.22 (2 H, dd, $^2J_{PH}$ 16, $^3J_{PH}$ 3, CH_2Ph), 7.3–7.4 (3 H, m, ArH), 7.45 (2 H, m, ArH); δ_C 30.61 (1 C, d, $^1J_{PC}$ 32, CH_2Ph), 32.41–32.92 (6 C, 10 lines complex multiplet), 134.16 (1 C, d, $^5J_{PC}$ 3, *para*-C), 135.11 (2 C, d, J_{PC} 3), 135.69 (2 C, d, J_{PC} 8), 135.99 (1 C, d, $^2J_{PC}$ 9, *ipso*-C); δ_P −54.24 (d, $^1J_{PP}$ 250, P-5), 86.05 (d, $^1J_{PP}$ 250, P-1); *m*/*z* (FAB^+) 237 (M^+ − Br, 100%). The title compound was reacted with a tenfold excess of sodium tetrafluoroborate in order to exchange the counter ion. Recrystallisation from CH_2Cl_2 and Et_2O furnished white crystals, mp 104–106 °C (Found: C, 48.0; H, 6.0. $C_{13}H_{19}BF_4P_2$ requires C, 48.2; H, 5.9%).

1-Benzyl-1-phosphonia-6-phosphabicyclo[4.4.0]decanium bromide 3e.Br. A solution of 1,6-diphosphabicyclo[4.4.0]decane (198 mg, 1.14 mmol) in Et_2O (10 cm^3) was treated with two

equivalents of benzyl bromide (0.27 cm^3, 2.3 mmol). The general procedure was as for the previous reaction and furnished a white solid (350 mg, 89%) mp 282–284 °C (Found: C, 52.0; H, 6.3. $C_{15}H_{23}BrP_2$ requires C, 52.2; H, 6.7%); $\delta_H(CD_2Cl_2)$ 1.6–1.8 (4 H, m), 1.8–2.0 (6 H, m), 2.0–2.2 (2 H, m), 2.63 (2 H, m), 2.90 (2 H, m), 4.34 (2 H, dd, $^2J_{PH}$ 15, $^3J_{PH}$ 6, CH_2Ph), 7.37 (3 H, m, ArH), 7.54 (2 H, m, ArH); δ_C 17.91 (2 C, d, $^1J_{PC}$ 33, C-5, C-7), 18.17 (2 C, dd, $^1J_{PC}$ 21, $^2J_{PC}$ 4, C-2, C-10), 21.17 (2 C, d, $^2J_{PC}$ 8, C-4, C-8), 21.82 (2 C, d, $^2J_{PC}$ 6, C-3, C-9), 29.63 (1 C, dd, $^1J_{PC}$ 39, $^2J_{PC}$ 9, *C*H_2Ph), 128.83 (1 C, d, $^5J_{PC}$ 4, *para*-C), 129.40 (1 C, d, $^2J_{PC}$ 9, *ipso*-C), 129.67 (2 C, d, $^4J_{PC}$ 3, *meta*-C), 130.64 (2 C, dd, $^3J_{PC}$ 6, $^4J_{PC}$ 2, *ortho*-C); δ_P −80.38 (d, $^1J_{PP}$ 257, P-6), −1.27 (d, $^1J_{PP}$ 257, P-1); *m*/*z* (FAB$^+$) 265 (M^+ − Br, 100%).

cis-Dialkyldiphosphacycloalkanes

***cis*-1,5-Dimethyl-1,5-diphosphacyclooctane 4a.** A suspension of 1-methyl-1-phosphonia-5-phosphabicyclo[3.3.0]octane trifluoromethanesulfonate (960 mg, 3.10 mmol) in Et_2O (20 cm^3), cooled to −78 °C, was treated with an excess of a solution of methyllithium in Et_2O (1.4 mol dm^{-3}, 4.5 cm^3, 6.3 mmol). The reaction mixture was warmed to room temperature to leave a homogeneous solution which was hydrolysed with water (0.25 cm^3). The solution was then dried (Na_2SO_4) and all volatiles were removed *in vacuo*. The resulting residue was extracted with light petroleum (bp 30–40 °C, 2 × 15 cm^3) and filtered through a glass sinter. Removal of all volatiles under high vacuum left a waxy white solid (420 mg, 77%); $\delta_H(CD_2Cl_2)$ 0.87 (6 H, t, N_{PH} 4, CH_3), 1.37 (4 H, m), 1.62 (4 H, m), 1.82 (2 H, m), 2.07 (2 H, m); δ_C 14.60 (2 C, t, N_{PC} 12, CH_3), 24.30 (2 C, t, $^2J_{PC}$ 14, C-3, C-7), 31.10 (4 C, t, N_{PC} 12, C-2, C-4, C-6, C-8); δ_P −39.63; *m*/*z* (CI) 161 ([M + 1]$^+$, 100%), 177 ([M + 1]$^+$ + O, 30). A small sample of *cis*-1,5-dimethyl-1,5-diphosphacyclooctane was sealed in an evacuated Schlenk tube, the bottom of which was submerged in an oil bath at 35 °C. Crystals suitable for X-ray crystal structure determination were grown by slow sublimation over two weeks.

***cis*-1-Benzyl-5-methyl-1,5-diphosphacyclooctane 4b.** A suspension of 1-benzyl-1-phosphonia-5-phosphabicyclo[3.3.0]-octane bromide (138 mg, 0.435 mmol) in Et_2O (10 cm^3) was treated with a solution of methyllithium in Et_2O (1.4 mol dm^{-3}, 0.75 cm^3, 0.91 mmol) at −78 °C. The general procedure and work-up were as previously described and furnished a white solid (86 mg, 77%) [Found (CI): M^+ + 1, 253.1283. $C_{14}H_{23}P_2$ requires 253.1275]; $\delta_H(CDCl_3)$ 0.90 (3 H, d, $^2J_{PH}$ 6, CH_3), 1.3–1.4 (4 H, m), 1.6–1.7 (2 H, m), 1.7–1.8 (2 H, m), 1.9–2.1 (4 H, m), 2.65 (2 H, d, $^2J_{PC}$ 2, CH_2Ph), 7.31 (5 H, m, ArH); δ_C 14.97 (1 C, dd, $^1J_{PC}$ 15, J_{PC} 7, *C*H_3), 25.00 (2 C, t, N_{PC} 28, C-3, C-7), 29.21 (2 C, d, $^1J_{PC}$ 25, C-2, C-8), 31.96 (2 C, d, $^1J_{PC}$ 15, C-4, C-6), 38.01 (1 C, dd, $^1J_{PC}$ 15, J_{PC} 5, *C*H_2Ph), 125.97 (1 C, s, *para*-C), 129.59 (2 C, s), 129.64 (2 C, d, J_{PC} 6), 139.10 (1 C, d, $^2J_{PC}$ 5, *ipso*-C); δ_P −40.24 (d, J_{PP} 36, P-5), −21.58 (d, J_{PP} 36, P-1); *m*/*z* (CI) 253 ([M + 1]$^+$, 21%), 269 ([M + 1]$^+$ + O, 100).

***cis*-1-Benzyl-5-phenyl-1,5-diphosphacyclooctane 4c.** A suspension of 1-benzyl-1-phosphonia-5-phosphabicyclo[3.3.0]-octane bromide (1.06 g, 3.34 mmol) in Et_2O (25 cm^3) was cooled to −78 °C and treated with a solution of phenyllithium in cyclohexane–Et_2O (7 : 3, 1.8 mol dm^{-3}, 0.50 cm^3, 0.90 mmol). The same general procedure as previously described yielded the title compound as a white solid (680 mg, 65%) [Found (CI): M^+ + 1, 315.1440. $C_{19}H_{25}P_2$ requires 315.1432); $\delta_H(CDCl_3)$ 1.2–1.3 (2 H, m), 1.3–1.5 (2 H, m), 1.6–1.7 (4 H, m), 1.8–2.1 (4 H, m), 2.52 (2 H, s, CH_2Ph), 7.1–7.5 (10 H, m, ArH); δ_C 24.42 (2 C, t, N_{PC} 28, C-3, C-7), 28.18 (2 C, d, $^1J_{PC}$ 25, C-2, C-8), 29.52 (2 C, d, $^1J_{PC}$ 15, C-4, C-6), 37.72 (1 C, dd, $^1J_{PC}$ 14, J_{PC} 6, *C*H_2Ph), 125.53 (1 C, d, $^5J_{PC}$ 3, benzyl-*para*-C), 126.95 (1 C, s, phenyl-*para*-C), 127.02 (2 C, d, J_{PC} 12, phenyl), 128.12 (2 C, s, benzyl), 128.58 (2 C, s, phenyl), 129.16 (2 C, d, J_{PC} 6, benzyl), 131.49 (1 C, d, $^1J_{PC}$ 18, phenyl-*ipso*-C), 138.12 (1 C, d, J_{PC} 5, benzyl-*ipso*-C); δ_P −23.69 (d, J_{PP} 56, P-5), −22.61 (d, J_{PP} 56, P-1); *m*/*z* (CI) 315 ([M + 1]$^+$, 3%), 238 ([M + 1]$^+$ − Ph, 98), 223 (M^+ − $PhCH_2$, 100).

***cis*-1,5-Dibenzyl-1,5-diphosphacyclooctane 4d.** A suspension of 1-benzyl-1-phosphonia-5-phosphabicyclo[3.3.0]octane bromide (2.50 g, 7.88 mmol) in Et_2O (60 cm^3) was cooled to −78 °C and treated with a solution of benzylmagnesium chloride in THF (2.0 mol dm^{-3}, 7.5 cm^3, 15 mmol). After warming to room temperature the reaction was stirred for one hour, with intermittent sonication to help dissolve the solids. The reaction mixture was quenched by the addition of water (0.30 cm^3), dried ($MgSO_4$), filtered through a glass sinter and the volatiles removed *in vacuo* to furnish a waxy solid (1.87 g, 72%) [Found (CI): M^+, 329.1586. $C_{20}H_{27}P_2$ requires 329.1588]; $\delta_H(CDCl_3)$ 1.3–1.4 (4 H, m), 1.6–1.7 (4 H, m), 1.7–1.9 (2 H, m), 1.9–2.2 (2 H, m), 2.61 (4 H, s, CH_2Ph), 7.0–7.4 (10 H, m, ArH); δ_C 24.66 (2 C, t, $^2J_{PC}$ 14, C-3, C-7), 28.51 (4 C, t, N_{PC} 17, C-2, C-4, C-6, C-8), 37.80 (2 C, dd, $^1J_{PC}$ 8, J_{PC} 3, *C*H_2Ph), 125.59 (1 C, s, *para*-C), 128.20 (2 C, s), 129.26 (2 C, t, N_{PC} 6), 138.28 (1 C, d, $^2J_{PC}$ 5, *ipso*-C); δ_P −22.40; *m*/*z* (CI) 329 ([M + 1]$^+$, 15%), 91 ($PhCH_2^+$, 55), 59 (100).

***cis*-1,6-Dimethyl-1,6-diphosphacyclononane 4e.** A suspension of 1-methyl-1-phosphonia-6-phosphabicyclo[4.3.0]nonane iodide (528 mg, 1.75 mmol) in Et_2O (10 cm^3), cooled to −78 °C, was treated with an excess of a solution of methyllithium in Et_2O (1.4 mol dm^{-3}, 2.5 cm^3, 3.5 mmol) and stirred. The procedure and work-up was as for the previous reaction and furnished a clear oil (283 mg, 85%) (Found (CI): M^+ + 1, 191.1128. $C_9H_{21}P_2$ requires 191.1118); $\delta_H(CDCl_3)$ 0.94 (6 H, d, $^2J_{PH}$ 3, CH_3), 1.33 (4 H, m), 1.4–1.7 (10 H, m); δ_C 12.22 (2 C, X part of an ABX system, N_{PC} 11, *C*H_3), 19.52 (1 C, t, $^2J_{PC}$ 7, C-8), 25.19 (2 C, X part of an AA′X system, N_{PC} 26, C-3, C4), 25.38 (2 C, X part of an ABX system, N_{PC} 16), 28.62 (2 C, X part of an ABX system, N_{PC} 10); δ_P −39.77; *m*/*z* (CI) 191 [M + 1]$^+$, 27%), 191 ([M + 1]$^+$ + O, 100).

***cis*-1,6-Dimethyl-1,6-diphosphacyclononane-1,6-disulfide.** *cis*-1,6-Dimethyl-1,6-diphosphacyclononane (150 mg, 0.79 mmol) in benzene (10 cm^3) was treated with sulfur (65 mg, 0.25 mmol) and heated at reflux for 20 hours. The solvent was removed *in vacuo* to leave a yellow residue which was extracted with CH_3CN (2 × 20 cm^3) and filtered to remove the excess sulfur. The solvent was removed to leave an off-white solid, which was recrystallised from acetonitrile and Et_2O (183 mg, 91%) mp 173–175 °C (Found: C, 42.5; H, 7.95. $C_9H_{20}P_2S_2$ requires C, 42.5; H, 7.9%); $\delta_H(CD_3CN)$ 1.62 (6 H, d, $^2J_{PH}$ 13, CH_3), 1.9–2.3 (14 H, m); δ_C 18.72 (1 C, t, $^2J_{PC}$ 5, C-8), 21.65 (2 C, d, $^1J_{PC}$ 46, *C*H_3), 22.14 (2 C, s, C-3, C-4), 31.85 (2 C, d, $^1J_{PC}$ 49), 34.06 (dd, $^1J_{PC}$ 47); δ_P 43.76. Slow diffusion of Et_2O into a saturated solution of the title compound in CH_2Cl_2 led to the formation of crystals suitable for X-ray structural determination.

***cis*-1,6-Dimethyl-1,6-diphosphacyclodecane 4f.** A suspension of 1-methyl-1-phosphonia-6-phosphabicyclo[4.4.0]decane iodide (351 mg, 1.11 mmol) in Et_2O (10 cm^3), cooled to −78 °C, was treated with an excess of methyllithium in Et_2O (1.4 mol dm^{-3}, 1.5 cm^3, 2.1 mmol). The procedure and work-up was as for the previous reactions and furnished a white solid (160 mg, 70%); $\delta_H(CDCl_3)$ 0.98 (6 H, d, $^2J_{PH}$ 3, CH_3), 1.49 (4 H, m), 1.5–1.8 (10 H, m); δ_C 12.30 (2 C, d, $^1J_{PC}$ 11, *C*H_3), 25.02 (4 C, dd, $^2J_{PC}$ 12 , $^3J_{PC}$ 8, C-3, C-5, C-7, C-10), 26.32 (4 C, d, $^1J_{PC}$ 15, C-3, C-4, C-8, C-9); δ_P −37.32. A small sample of the title compound was placed in an evacuated Schlenk tube, the bottom of which was placed in an oil bath at 40 °C in a room held at 4 °C. After two weeks crystals suitable for an X-ray crystal structure determination had formed on the upper regions of the tube.

***cis*-1,6-Dibenzyl-1,6-diphosphacyclodecane 4g.** A suspension of 1-benzyl-1-phosphonia-6-phosphabicyclo[4.4.0]decane bromide (700 mg, 2.03 mmol) in THF (60 cm^3) was cooled to −78 °C and treated with a solution of benzylmagnesium chloride in THF (2.0 mol dm^{-3}, 2.0 cm^3, 4.0 mmol). After warming to room temperature the reaction was stirred for one hour, with intermittent sonication to help dissolve the solids. The reaction mixture was quenched by the addition of water (0.30 cm^3), then dried ($MgSO_4$) and the volatiles removed *in vacuo*. The resulting

residue was extracted with light petroleum (bp 30–40 °C, 2 × 20 cm^3), filtered through a glass sinter and evaporated to dryness to furnish a waxy solid (610 mg, 84%) [Found (CI): $M^+ + 1$, 357.1888. $C_{22}H_{31}P_2$ requires 357.1901]; $\delta_H(CDCl_3)$ 1.4–1.7 (16 H, m), 2.69 (4 H, s, CH_2Ph), 7.10 (6 H, m, ArH), 7.18 (4 H, m, ArH); δ_C 24.15 (4 C, d, $^1J_{PC}$ 14, C-2, C-5, C-7, C-10), 25.28 (4 C, X part of an AA′X system, N_{PC} 5, C-3, C-4, C-8, C-9), 35.47 (2 C, X part of an ABX system, N_{PC} 12, *C*H_2Ph), 125.57 (1 C, s, *para*-C), 128.26 (2 C, s), 128.97 (2 C, d, J_{PC} 6), 138.47 (1 C, d, $^2J_{PC}$ 5, *ipso*-C); δ_P −18.99; *m*/*z* (CI) 357 ([M + 1]$^+$, 60%), 265 ([M + 1]$^+$ − $PhCH_2$, 100).

Dialkylated 1,*k* + 2-diphosphabicyclo[*k*.*l*.0]alkanes

***cis*-1,5-Dimethyl-1,5-diphosphoniabicyclo[3.3.0]octane bis(trifluoromethanesulfonate) 5a.** To a stirred solution of 1-methyl-1-phosphonia-5-phosphabicyclo[3.3.0]octane iodide (118 mg, 0.41 mmol) in CH_2Cl_2 (5 cm^3) was added methyl trifluoromethanesulfonate (130 mg, 0.82 mmol). The solution cleared instantly. After five minutes, solids began to form in the solution. After three hours, the solids were allowed to settle and the colourless solution was decanted away. The solids were washed (1 × 5 cm^3 CH_2Cl_2) and dried under high vacuum to leave an extremely hygroscopic, white crystalline powder (170 mg, 87%) mp 130–135 °C (Found: C, 24.6; H, 3.8. $C_{10}H_{18}F_6O_6P_2S_2$ requires C, 25.3; H, 3.8%); $\delta_H(CD_3CN)$ 1.95 (2 H, m), 2.30 (6 H, m), 2.60 (6 H, m), 2.82 (4 H, m); δ_C 6.25 (2 C, t, N_{PC} 41, *C*H_3), 25.15 (2 C, d, $^2J_{PC}$ 6, C-2, C-5), 26.19 (4 C, t, N_{PC} 51, C-1, C-3, C-4, C-6); δ_P 54.00.

***cis*-1,6-Dimethyl-1,6-diphosphoniabicyclo[4.3.0]nonane bis(trifluoromethanesulfonate) 5b.** A stirred solution of *cis*-1,6-diphosphabicyclo[4.3.0]nonane (77 mg, 0.48 mmol) in CH_2Cl_2 (4 cm^3), at 0 °C, was treated with methyl trifluoromethanesulfonate (160 mg, 0.98 mmol). The mixture was allowed to warm to room temperature. After one hour, solids began to appear in solution. After stirring overnight, solvent and volatiles were removed under high vacuum to leave a colourless hygroscopic solid in quantitative yield (Found: C, 26.5; H, 4.6. $C_{11}H_{20}F_6O_6P_2S_2$ requires C, 27.05; H, 4.1%); $\delta_H(CD_3CN)$ 1.90–2.30 (4 H, m), 2.50–2.70 (8 H, m), 2.90–3.20 (8 H, m); δ_C 6.23 (2 C, t, N_{PC} 39, *C*H_3), 19.59 (2 C, s, C-2, C-3), 21.53 (2 C, t, N_{PC} 34, C-5, C-7), 23.81 (1 C, s, C-6), 26.36 (2 C, t, N_{PC} 51, C-1, C-4); δ_P 25.86.

***cis*-1,6-Dimethyl-1,6-diphosphoniabicyclo[4.4.0]decane bis(trifluoromethanesulfonate) 5c.** A stirred solution of *cis*-1,6-diphosphabicyclo[4.4.0]decane (19 mg, 0.1 mmol) in CD_3CN (0.5 cm^3) was treated with methyl trifluoromethanesulfonate (35 mg, 0.2 mmol). The mixture was analysed by NMR, without isolation of the product; $\delta_H(CD_3CN)$ 1.60 (8 H, m), 1.95 (6 H, d, $^2J_{PH}$ 10, CH_3), 2.45 (8 H, m); δ_C 3.75 (2 C, t, N_{PC} 41, *C*H_3), 19.42 (4 C, t, N_{PC} 34, C-1, C-4, C-5, C-8), 20.24 (4 C, s, C-2, C-3, C-6, C-7); δ_P 4.07.

***trans*-Dialkyldiphosphacycloalkane mono-oxides**

***trans*-1,5-Dimethyl-1-hydroxy-1,5-diphosphoniacyclooctane bis(trifluoromethanesulfonate).** To a stirred solution of *cis*-1,5-dimethyl-1,5-diphosphoniabicyclo[3.3.0]octane bis(trifluoromethanesulfonate) (250 mg, 0.6 mmol) in acetonitrile (2 cm^3) was added water (10 mg, 0.6 mmol). After five minutes, the solvent was removed *in vacuo* to leave a solid residue, which was recrystallised from acetonitrile and CH_2Cl_2 and dried under high vacuum to give a crystalline solid in quantitative yield mp 150–155 °C (Found: C, 24.3; H, 4.1. $C_{10}H_{20}F_6O_7P_2S_2$ requires C, 24.4; H, 4.1%); $\delta_H(CD_3CN)$ 0.98 (3 H, dd, $^2J_{PH}$ 15, $^3J_{HH}$ 5, CH_3PH), 1.37 [3 H, d, $^2J_{PH}$ 13, CH_3P(OH)], 2.10 (4 H, m), 2.50 (8 H, m), 6.25 (1 H, d, $^1J_{PH}$ 504, P*H*), 11.40 (1 H, s, PO*H*); δ_C 4.27 (1 C, d, $^1J_{PC}$ 53, *C*H_3PH), 13.64 (1 C, d, $^1J_{PC}$ 64, *C*H_3POH), 14.58 (2 C, t, $^2J_{PC}$ 6, C-2, C-5), 18.38 (2 C, d, $^1J_{PC}$ 47, C-3, C-4), 25.28 (2 C, d, $^1J_{PC}$ 61, C-1, C-6); δ_P 84.60 (P-1), 5.30 (d, $^1J_{PH}$ 505, P-5).

***trans*-1,5-Dimethyl-1,5-diphosphacyclooctane-1-oxide 6a.** To a stirred solution of *cis*-1,5-dimethyl-1,5-diphosphoniabicyclo[3.3.0]octane bis(trifluoromethanesulfonate) (370 mg, 0.79 mmol) in acetonitrile (3 cm^3) was added water (15 mg, 0.79 mmol). After five minutes, an aqueous solution of sodium hydroxide (5 mol dm^{-3}, 0.38 cm^3, 1.9 mmol) was added. After stirring for a further two hours, solvent and volatiles were removed under high vacuum to leave a solid residue, which was extracted (2 × 5 cm^3 CH_2Cl_2) and filtered through a glass sinter. Removal of solvent *in vacuo* left a colourless, sticky solid which could not be recrystallised (146 mg, 97%); $\delta_H(CH_2Cl_2)$ 0.98 [3 H, d, $^2J_{PH}$ 6, CH_3P(CH_2)$_2$], 1.37 [3 H, d, $^2J_{PH}$ 18, CH_3PO(CH_2)$_2$], 1.6–1.9 (8 H, m), 2.0–2.3 (4 H, m); δ_C 13.13 [1 C, d, $^1J_{PC}$ 9, *C*H_3P(CH$_2$)$_2$], 16.58 [1 C, d, $^1J_{PC}$ 68, *C*H_3PO(CH$_2$)$_2$], 18.39 (2 C, dd, $^2J_{PC}$ 12, $^2J_{PC}$ 3, C-2, C-5), 29.47 (2 C, dd, $^1J_{PC}$ 64, $^3J_{PC}$ 9, C-1, C-6), 29.56 (2 C, dd, $^1J_{PC}$ 11, $^3J_{PC}$ 3, C-3, C-4); δ_P 46.81 (P-1), −42.22 (P-5); *m*/*z* (EI) 192 (M^+, 1%), 177 (100), 135 (7).

***trans*-1,5-Dimethyl-1,5-diphosphacyclooctane-1-oxide-5-sulfide.** A solution of *trans*-1,5-dimethyl-1,5-diphosphacyclooctane-1-oxide (44 mg, 0.23 mmol) in benzene (2 cm^3) was treated with sulfur (7 mg, 0.23 mmol), then heated to reflux for one hour. On cooling to room temperature, the solvent was removed *in vacuo* to leave a white, sticky solid in quantitative yield [Found (EI): 224.0540. $C_8H_{18}OP_2S$ requires 224.0554]; $\delta_H(CD_2Cl_2)$ 1.40 (3 H, d, $^2J_{PH}$ 13, CH_3PO), 1.62 (3 H, d, $^2J_{PH}$ 12, CH_3PS), 2.00 (10 H, m), 2.50 (2 H, m); δ_C 15.75 (2 C, s, C-2, C-5), 17.96 (1 C, d, $^1J_{PC}$ 68, *C*H_3PO), 21.61 (1 C, d, $^1J_{PC}$ 56, *C*H_3PS), 29.71 (2 C, d, $^1J_{PC}$ 63, C-1, C-6), 32.77 (2 C, d, $^1J_{PC}$ 48, C-3, C-4); δ_P 45.48 (P-1), 41.51 (P-5); *m*/*z* (EI) 224 (M^+, 23%), 192 (15).

***trans*-1,6-Dimethyl-1-hydroxy-1,6-diphosphoniacyclononane bis(trifluoromethanesulfonate).** To *cis*-1,6-dimethyl-1,6-diphosphoniabicyclo[4.3.0]nonane bis(trifluoromethanesulfonate) (0.19 g, 0.4 mmol) dissolved in acetonitrile (2 cm^3) was added water (8 mg, 0.4 mmol). After stirring for five minutes, solvent and volatiles were removed *in vacuo* to leave an oily residue, which was recrystallised from acetonitrile and dichloromethane and dried under high vacuum to give a white solid (Found: C, 26.1; H, 4.6. $C_{11}H_{22}F_6O_7P_2S_2$ requires C, 26.1; H, 4.4%); $\delta_H(CD_3CN)$ 1.70 (10 H, m), 2.25 (10 H, m), 6.10 (1 H, d, $^1J_{PH}$ 504, P*H*), 11.00 (1 H, s, PO*H*); δ_C 4.00 (1 C, d, $^1J_{PC}$ 51, *C*H_3PH), 13.11 [1 C, d, $^1J_{PC}$ 64, *C*H_3P(OH)], 14.52 (1 C, t, $^2J_{PC}$ 6, C-6), 16.78 (1 C, d, $^1J_{PC}$ 47, C-5), 19.74 (1 C, s, C-3), 20.08 (1 C, dd, $^1J_{PC}$ 47, $^3J_{PC}$ 4, C-4), 21.67 (1-C, t, $^2J_{PC}$ 4, C-3), 23.96 (1 C, d, $^1J_{PC}$ 61, C-1), 26.13 (1 C, d, $^1J_{PC}$ 62, C-7); δ_P 86.30 (P-1), 7.84 (d, $^1J_{PH}$ 504, P-5).

***trans*-1,6-Dimethyl-1,6-diphosphacyclononane-1-oxide 6b.** A stirred solution of *cis*-1,6-dimethyl-1,6-diphosphoniabicyclo[4.3.0]nonane bis(trifluoromethanesulfonate) (136 mg, 0.27 mmol) in acetonitrile (3 cm^3) was treated with water (5 mg, 0.27 mmol). After five minutes, aqueous NaOH was added (4 mol dm^{-3}, 0.14 cm^3, 0.54 mmol). After two hours, solvent and volatiles were removed *in vacuo*. The resulting residue was extracted with CH_2Cl_2 (2 × 5 cm^3) and filtered through a glass sinter, removal of solvent *in vacuo* leaving a sticky solid (0.047 g, 84%) [Found (EI): 191.0772. $C_8H_{17}OP_2$ (M − CH_3) requires 191.0755]; $\delta_H(CD_2Cl_2)$ 1.00 [3 H, d, $^2J_{PH}$ 5, CH_3P(CH_2)$_2$], 1.40 (3 H, d, $^2J_{PH}$ 15, CH_3PO), 1.5–2.3 (14 H, m); δ_C 14.11 [1 C, d, $^1J_{PC}$ 12, *C*H_3P(CH$_2$)$_2$], 14.90 (1 C, d, $^1J_{PC}$ 68, *C*H_3PO), 18.41 (1 C, d, $^1J_{PC}$ 17, C-6), 21.45 (1 C, d, $^2J_{PC}$ 4, C-3), 25.35 (1 C, dd, $^2J_{PC}$ 5, $^3J_{PC}$ 12, C-5), 26.51 (1 C, dd, $^1J_{PC}$ 67, $^2J_{PC}$ 7, C-1), 28.64 (1 C, d, $^2J_{PC}$ 14, C-2), 28.73 (1 C, dd, $^1J_{PC}$ 66, $^3J_{PC}$ 9, C-7), 31.53 (d, $^1J_{PC}$ 14, C-4); δ_P 52.12 (P-1), −43.13 (P-6); *m*/*z* (EI) 206 (M^+, 0.8%), 191 (100), 163 (27), 135 (10).

***trans*-1,6-Dimethyl-1,6-diphosphacyclononane-1,6-dioxide.** A stirred solution of *trans*-1,6-dimethyl-1,6-diphosphacyclononane (48 mg, 0.25 mmol) in CH_2Cl_2 (2 cm^3) at 0 °C was treated with an aqueous solution of H_2O_2 (30%, 0.02 cm^3). After one day, volatiles were removed *in vacuo* to leave a colourless oil in quantitative yield [Found (EI): 222.0946. $C_9H_{20}O_2P_2$ requires 222.0938]; $\delta_H(CD_3CN)$ 1.30 (6 H, d, $^2J_{PH}$ 20, CH_3), 1.5–2.0 (14

Table 5 Details of structure analyses

Compounds	**2b.S_2**	**2c.S_2**	**3a.I**	**3b.I**	**3c.I**
Crystal data[a]					
Formula	$C_7H_{14}P_2S_2$	$C_8H_{16}P_2S_2$	$C_7H_{15}IP_2$	$C_8H_{17}IP_2$	$C_9H_{19}IP_2$
M	224.2	238.3	288.1	302.1	316.1
Crystal system	Orthorhombic	Monoclinic	Orthorhombic	Orthorhombic	Orthorhombic
Space group (No.)	*Pbca* (No. 61)	*C*2/*c* (No. 15)	$P2_12_12_1$ (No. 19)	$Pna2_1$ (No. 33)	*Pbca* (No. 61)
a (Å)	12.809(5)	14.622(4)	7.032(1)	10.364(1)	10.513(2)
b	12.258(5)	6.646(2)	11.166(2)	12.450(2)	16.833(4)
c	13.684(4)	13.536(4)	13.613(3)	9.294(1)	28.942(5)
β (°)	90	117.57(2)	90	90	90
U (Å^3)	2148.6(14)	1166.0(6)	1068.9(3)	1199.3(3)	5122(2)
Z	8	4	4	4	16
D_c (g cm^{-3})	1.39	1.36	1.79	1.67	1.64
F(000)	944	504	560	592	2496
μ(Mo-Kα) (cm^{-1})	7.35	6.81	32.0	28.5	27.1
Data collection and reduction					
Crystal dimensions (mm)	0.43 × 0.25 × 0.18	0.20 × 0.40 × 0.40	0.45 × 0.45 × 0.35	0.3 × 0.2 × 0.2	0.20 × 0.35 × 0.40
2*θ* range (°)	3–45	3–60	4–52	4–50	3–45
Scan method	*ω* Wyckoff	*ω*–2*θ*	*ω*–2*θ*	*ω*–2*θ*	*ω* Wyckoff
Total data	1654	1936	1353	1347	4248
Unique data	1406	1713	1353	1347	3732
'Observed' data (NO)	945	1401	1183	964	2489
Min., max. transmission coefft.	0.624, 0.916	0.866, 1.00	0.209, 0.299	0.270, 0.306	0.619, 0.802
Refinement					
Least squares variables (NV)	100	56	91	99	217
R	0.057[b]	0.029[b]	0.022[b]	0.030[b]	0.034[b]
wR	0.056[b]	0.034[b]	0.030[b]	0.034[b]	0.033[b]
S	1.34[b]	1.32[b]	1.51[b]	1.07[b]	1.05[b]
g	0.0011	0.0005	0.0002	0.0003	0.0005
Final difference map features (e Å^{-3})	+0.50, −0.39	+0.28, −0.23	+0.52, −0.38	+1.28, −0.34	+0.40, −0.43

[a] Data common to all: $T = 293$ K; wavelength 0.710 73 Å, observation criterion $[F_o^2 > 2\sigma(F_o^2)]$. [b] $R = \Sigma|\Delta|/\Sigma|F_o|$; $wR = [\Sigma w\Delta^2/\Sigma wF_o^2]^{1/2}$; $S = [\Sigma w\Delta^2/(NO - NV)]^{1/2}$; $\Delta = F_o - F_c$; $w = [\sigma_c^2(F_o) + gF_o^2]^{-1}$, $\sigma_c^2(F_o)$ = variance in F_o due to counting statistics.

H, m); δ_C 15.00 (1 C, C-6), 16.81 (2 C, d, $^1J_{PC}$ 70, *C*H$_3$), 21.14 (2 C, C-2, C-3), 28.25 (2 C, d, $^1J_{PC}$ 65, C-1, C-4), 30.23 (2 C, d, $^1J_{PC}$ 63, C-5, C-7); δ_P 50.16; *m*/*z* (EI) 222 (M$^+$, 14%), 207 (100), 179 (55).

***trans*-1,6-Dimethyl-1-hydroxy-1,6-diphosphoniacyclononane bis(trifluoromethanesulfonate).** The above sample was treated with water (2 mg, 0.11 mmol). Solvent and volatiles were removed *in vacuo* to leave a white solid mp 145–150 °C (Found: C, 28.2; H, 5.0. $C_{12}H_{24}F_6O_7P_2S_2$ requires C, 27.6; H, 4.7%); $\delta_H(CD_3CN)$ 1.90 (14 H, m), 2.42 (8 H, m), 6.30 (1 H, d, $^1J_{PH}$ 503, P*H*), 10.50 (1 H, br, PO*H*); δ_C 2.89 [1 C, d, $^1J_{PC}$ 51, *C*H$_3$P(CH$_2$)$_2$], 12.16 [1 C, d, $^1J_{PC}$ 60, *C*H$_3$PO(CH$_2$)$_2$], 15.88 (2 C, d, $^1J_{PC}$ 46, C-4, C-5), 20.07 (2 C, d, $^2J_{PC}$ 9, C-2, C-7), 20.92 (2 C, m, C-3, C-6), 23.41 (2 C, d, $^1J_{PC}$ 61, C-1, C-8); δ_P 86.50 (P-1), 7.68 (d, $^1J_{PH}$ 503, P-6).

***trans*-1,6-Dimethyl-1,6-diphosphacyclodecane-1-oxide 6c.** A stirred solution of *cis*-1,6-dimethyl-1,6-diphosphoniabicyclo-[4.4.0]decane bis(trifluoromethanesulfonate) (156 mg, 0.31 mmol) in acetonitrile (2 cm^3) was treated with water (6 mg, 0.31 mmol). After five minutes, an aqueous NaOH solution (4 mol dm^{-3}, 0.20 cm^3, 0.80 mmol) was added. After one hour, solvent and volatiles were removed *in vacuo*, and the residue extracted with CH_2Cl_2 (2 × 5 cm^3). Removal of solvent left a colourless solid (59 mg, 87%); $\delta_H(CD_3CN)$ 1.55 [3 H, d, $^2J_{PH}$ 2, C*H*$_3$P(CH$_2$)$_2$], 1.51 (3 H, d, $^2J_{PH}$ 12, C*H*$_3$PO), 1.60–2.10 (16 H, m); δ_C 11.19 [1 C, d, $^1J_{PC}$ 9, *C*H$_3$P(CH$_2$)$_2$], 15.52 (1 C, d, $^1J_{PC}$ 65, *C*H$_3$PO), 21.07 (2 C, C-3, C-6), 23.40 (2 C, t, $^2J_{PC}$ 7, $^3J_{PC}$ 7, C-2, C-7), 23.97 (2 C, d, $^1J_{PC}$ 17, C-4, C-5), 26.68 (2 C, d, $^1J_{PC}$ 63, C-1, C-8); δ_P 52.29 (P-1), −37.91 (P-6).

***trans*-1,6-Dimethyl-1,6-diphosphacyclodecane-1,6-dioxide.** A stirred solution of *trans*-1,6-dimethyl-1,6-diphosphacyclodecane-1-oxide (59 mg, 0.27 mmol) in acetonitrile (2 cm^3) was treated with an aqueous solution of H_2O_2 (30%; 0.03 cm^3). After one day, solvent and volatiles were removed *in vacuo* to leave a solid residue which was recrystallised from methanol and Et$_2$O to give a colourless solid (0.047 g, 77%) mp 200–210 °C [Found: 221.0867. $C_9H_{19}O_2P_2$ (M − CH$_3$) requires 221.0860]; $\delta_H(CD_3OD)$ 1.41 (6 H, d, $^2J_{PH}$ 12, C*H*$_3$), 1.65 (4 H, m), 1.90 (12 H, m); δ_C 15.71 (2 C, d, $^1J_{PC}$ 65, *C*H$_3$), 22.10 (4 C, d, $^2J_{PC}$ 7, C-2, C-3, C-5, C-6), 27.21 (4 C, d, $^1J_{PC}$ 63, C-1, C-4, C-5, C-6); δ_P 55.52; *m*/*z* (EI) 236 (M$^+$, 11%), 221 (100), 193 (35).

***trans*-Dialkyldiphosphacycloalkanes**

***trans*-1,5-Dimethyl-1,5-diphosphacyclooctane 7a.** To a stirred solution of *trans*-1,5-dimethyl-1,5-diphosphacyclooctane-1-oxide (16 mg, 0.8 mmol) in Et$_2$O (4 cm^3) and benzene (2 cm^3), at 0 °C, was added $LiAlH_4$ (63 mg, 1.7 mmol). The reaction mixture was heated to reflux overnight, then cooled to 0 °C, treated carefully with aqueous NaOH (5 mol dm^{-3}, 0.5 cm^3, 2.5 mmol) and stirred for a further 30 minutes at room temperature. The solution was dried (anhydrous Na_2SO_4), then filtered through a glass sinter. Removal of solvent *in vacuo* left a colourless oil (61 mg, 43%); δ_H 0.82 (6 H, d, $^2J_{PH}$ 6, C*H*$_3$), 1.42 (4 H, m), 1.53 (4 H, m) 1.83 (4 H, m); δ_C 12.82 (2 C, d, $^1J_{PC}$ 12, *C*H$_3$), 21.51 (2 C, t, $^2J_{PC}$ 10, C-2, C-5), 28.84 (4 C, dd, $^1J_{PC}$ 15, $^3J_{PC}$ 6, C-1, C-3, C-4, C-6); $\delta_P(CD_2Cl_2)$ −39.43; *m*/*z* (EI) 176 (M$^+$, 22.6%), 161 (55).

***trans*-1,6-Dimethyl-1,6-diphosphacyclononane 7b.** To a stirred suspension of *trans*-1,6-dimethyl-1,6-diphosphacyclononane-1-oxide (127 mg, 0.62 mmol) in Et$_2$O (5 cm^3) at 0 °C was added $LiAlH_4$ (46 mg, 1.2 mmol). The mixture was heated to reflux for two days. On cooling to 0 °C, aqueous NaOH (4 mol dm^{-3}, 0.5 cm^3, 2 mmol) was added and the mixture left to stir for 30 minutes. Anhydrous Na_2SO_4 was used to dry the solution, which was filtered through a glass sinter and solvent removed under high vacuum to leave a colourless oil (73 mg, 61%); $\delta_H(CD_2Cl_2)$ 0.93 (6 H, d, $^2J_{PH}$ 6, C*H*$_3$), 1.5 (6 H, m), 1.7–2.0 (8 H, m); δ_C 12.99 (2 C, d, $^1J_{PC}$ 12, C-1, C-4), 22.57 (1 C, t, $^2J_{PC}$ 11, C-6), 25.15 (2 C, t, $^2J_{PC}$ 9, C-2, C-3), 27.94 (2 C, dd, $^1J_{PC}$ 15, $^3J_{PC}$ 4, C-5, C-7), 29.98 (2 C, dd, $^1J_{PC}$ 15, $^3J_{PC}$ 4, C-2, C-3); δ_P −40.64.

X-Ray experimental structures of 1,6-diphosphabicyclo[4.3.0]-nonane-1,6-dithione 2b.S_2, 1,6-diphosphabicyclo[4.4.0]decane-1,6-dithione 2c.S_2, 1-methyl-1-phosphonia-5-phosphabicyclo-[3.3.0]octane iodide 3a.I, 1-methyl-1-phosphonia-6-phospha-bicyclo[4.3.0]nonane iodide 3b.I and 1-methyl-1-phosphonia-6-phosphabicyclo[4.4.0]decane iodide 3c.I

Many of the details of the structure analyses carried out on compounds **2b.S_2**, **2c.S_2**, **3a.I**, **3b.I** and **3c.I** are listed in Table 5.† X-ray diffraction measurements were made at room temperature using Siemens four-circle R3m/V diffractometers on single crystals mounted in thin-walled glass capillaries with graphite monochromated Mo-Kα X-radiation. Cell dimensions for each analysis were determined from the setting angle values of centred reflections.

For each structure analysis intensity data were collected for unique portions of reciprocal space and corrected for Lorentz, polarisation, crystal decay and long-term intensity fluctuations, on the basis of the intensities of three check reflections repeatedly measured during data collection. Corrections for X-ray absorption effects were applied on the basis of azimuthal scan data. The structures were solved by direct methods, and refined by full-matrix least-squares against *F*. All non-hydrogen atoms were assigned anisotropic displacement parameters and refined without positional constraints or restraints. Molecules of **2c.S_2** lie at sites of crystallographic two-fold symmetry. All hydrogen atoms were constrained to ideal geometries with C–H = 0.96 Å and assigned fixed isotropic displacement parameters. An isotropic extinction correction was applied in the case of **2c.S_2**, parameter x refined to 0.0167(7) where $F_c = F_c^{\text{uncorr.}}/(1 + 0.002\, xF_c^2/\sin 2\theta)^{1/4}$. For **3a.I** and **3b.I** the absolute structure was confirmed by refinement.[30] In the structure of **3c.I** there are two similar cations and two iodide anions present in the asymmetric unit. The C–C bond lengths (which are short), C–C–C angle (which is large) and displacement parameters (which are large) of C(6) which is in the C_3 bridge in **2b.S_2** show signs of local disorder.

Final difference syntheses showed no chemically significant features. Refinements converged smoothly to residuals given in Table 5. Full tables of positional parameters, interatomic distances and bond angles, displacement parameters, hydrogen atomic parameters and observed and calculated structure amplitudes are given in the supplementary material.

Calculations were made with programs of the SHELXTL-PLUS[31] package as implemented on a Siemens R3m/V structure determination system. Complex neutral-atom scattering factors were taken from ref. 32.

Photoelectron spectra

He(I) photoelectron spectra of **2a**, **2b** and **4a** were recorded at room temp. and **2c** and **4f** at 38 °C with a Perkin-Elmer PS18 instrument. Calibration was with Ar and Xe, with resolution of 0.2 meV on the $^2P_{3/2}$ line of Ar.

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† Full crystallographic details, excluding structure factor tables, have been deposited at the Cambridge Crystallographic Data Centre (CCDC). For details of the deposition scheme, see 'Instructions for Authors', *J. Chem. Soc., Perkin Trans. 1*, available *via* the RSC Web page (http://www.rsc.org/authors). Any request to the CCDC for this material should quote the full literature citation and the reference number 207/205.