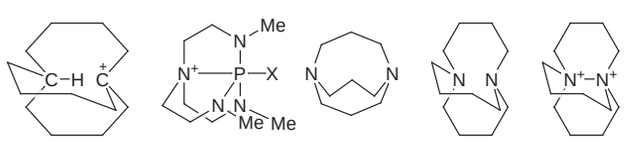
Bridgehead diphosphines in the bicyclo[3.3.3]undecane and bicyclo[4.4.4]tetradecane series: synthesis, structure and properties

Roger W. Alder,*,[a] Dianne D. Ellis,[a] Rolf Gleiter,[b] Christopher J. Harris,[a] Holger Lange,[b] A. Guy Orpen,[a] David Read[a] and Peter N. Taylor[a]

[a] *School of Chemistry, University of Bristol, Cantock's Close, Bristol, UK BS8 1TS*
[b] *Organisch-Chemische Institut, Universität Heidelberg, Im Neuenheimer Feld 270, D-69120 Heidelberg, Germany*

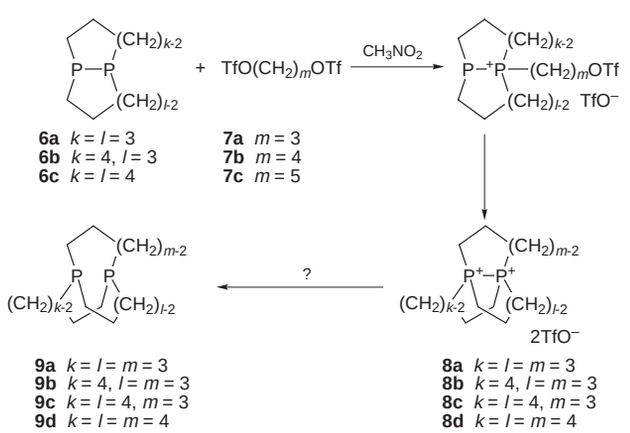
Several propellane diphosphonium salts 8 are prepared by the reaction of 1,*k* + 2-diphosphabicyclo-[*k.l.*0]alkanes 6 with α,ω-alkanediol bis-triflates [bis(trifluoromethanesulfonates)]; their properties are strongly dependent on ring size. 1,6-Diphosphoniatricyclo[4.4.4.0]tetradecane bis-triflate 8d is stable in acidic aqueous solution, and reacts with nucleophiles [X = F^-, MeO^-, H^- (from BH_4^-) and R^- (from Grignard and alkyllithium reagents)] to give products 13–18 with partial X–P–P^+ bonding, hydroxide ion gives the diphosphine monooxide 12b but even this may retain some P–P bonding. However 1,5-diphosphoniatricyclo[3.3.3.0]undecane bis-triflate 8a is hydrolysed irreversibly and much more rapidly than its [4.4.4.0] counterpart. 1,6-Diphosphoniatricyclo[4.4.3.0]tridecane bis-triflate 8c reacts with $NaBH_4$ to give a hydride adduct 15a which is deprotonated by Bu^{n}Li to give 1,6-diphosphabicyclo[4.4.3]tridecane 9c. However several attempts to prepare 1,6-diphosphabicyclo[4.4.4]tetradecane 9d led to a deep-seated rearrangement to give 1,4-bis(1-phospholan-1-yl)butane. These included reaction of hydride adduct 15b with Bu^{n}Li, and debenzylations of 1-benzyl-1-phosphonia-6-phosphabicyclo[4.4.4]tetradecane trifluoromethanesulfonate 16b and 1,6-dibenzyl-1,6-diphosphoniabicyclo[4.4.4]tetradecane bromide triflate 21 with $LiAlH_4$. Reaction of *cis*-1,5-dibenzyl-1,5-diphosphacyclooctane with $CH_2(CH_2OTf)_2$ gives 1,5-dibenzyl-1,5-diphosphoniabicyclo[3.3.3]undecane bis-triflate which is debenzylated with $LiAlH_4$ to 1,5-diphosphabicyclo[3.3.3]undecane 9a. Attempts to prepare 1,6-diphosphabicyclo[4.4.4]tetradecane by related methods lead to oligomerisation reactions. The structure of 1,5-diphosphabicyclo[3.3.3]-undecane is reported; its He(I) photoelectron spectrum shows two well separated bands at 7.58 and 8.14 eV, and RHF/6-31G* *ab initio* calculations indicating that this is due to through-bond interactions.

The interactions between bridgehead atoms in medium-ring bicyclic compounds have provided stable examples of a number of unusual types of bonding. Thus McMurry has shown that several highly stable carbocations, *e.g.* **1**, with μ-hydrido bridging can be generated[1] and Verkade has demonstrated a gradation of hypervalent P···N interactions in compounds like **2**.[2] Our own work[3] has been largely concerned with nitrogen



1 **2** **3** **4** **5**

bridgeheads in compounds such as 1,5-diazabicyclo[3.3.3]-undecane[4] **3** and 1,6-diazabicyclo[4.4.4]tetradecane[5] **4**. Since these medium-ring bicyclic compounds are severely strained, many have been prepared by indirect routes involving ring expansion or cleavage, *e.g.* **4** was obtained by reductive cleavage of **5**. In extending these studies to phosphorus, we reported the preparation of 1,6-diphosphoniatricyclo[4.4.4.0]tetradecane bis-triflate **8d** (Scheme 1) by alkylation of 1,6-diphosphabicyclo-[4.4.0]decane **6c** with $(CH_2CH_2OTf)_2$ **7b** in acetonitrile, but found that this compound could not be reduced to 1,6-diphosphabicyclo[4.4.4]tetradecane **9d**.[6] We have substantially improved the preparation of **8d**, and these improvements have permitted us to prepare several lower homologues.[7,8] In this paper, we describe these methods in detail. We have also found that we can gain access to 1,5-diphosphabicyclo[3.3.3]undecane by a reaction which simultaneously closes two eight-membered



6a *k* = *l* = 3
6b *k* = 4, *l* = 3
6c *k* = *l* = 4

7a *m* = 3
7b *m* = 4
7c *m* = 5

9a *k* = *l* = *m* = 3
9b *k* = 4, *l* = *m* = 3
9c *k* = *l* = 4, *m* = 3
9d *k* = *l* = *m* = 4

8a *k* = *l* = *m* = 3
8b *k* = 4, *l* = *m* = 3
8c *k* = *l* = 4, *m* = 3
8d *k* = *l* = *m* = 4

Scheme 1

rings with surprising ease. The structure and properties of these compounds and their derivatives will also be discussed.

Results and discussion

Preparation of propellane 1,*k* + 2-diphosphoniatricyclo-[*k.l.m.*0]alkane bis-triflates

We have described the preparation of a range of *cis*-1,*k* + 2-diphosphabicyclo[*k.l.*0]alkanes **6** in the accompanying paper.[9] We hoped that these compounds would be useful substrates for cycloalkylation to generate propellane dications (1,*k* + 2-diphosponiatricyclo[*k.l.m.*0]alkane dications) which might be reduced to generate 1,*k* + 2-diphosphabicyclo[*k.l.m*]alkanes,

using procedures based on earlier work with the corresponding nitrogen compounds.[10,11] This general approach has the major virtue that all the ring closures involve the formation of common-sized (*e.g.* six-membered) rings, and the medium-rings in the final products are created in the final reduction step. In the nitrogen series all the oxidation states are isolable, and we hoped that this would be the case with the diphosphines. Since barriers to inversion of phosphines are generally quite high, the diphosphines might exist in separable *in*,*in*, *in*,*out* and *out*,*out* forms;[12] the corresponding diamines are of course free to invert and adopt whichever is the most stable form (the *in*,*in*-isomer in the case of **4**).[13] Molecular mechanics calculations suggest that *in*,*in*-isomers of diphosphines with ring systems smaller than bicyclo[5.5.5]heptadecane would have very short P···P distances and therefore be extremely strained, but the other two isomers might have comparable strain energies.

Monoalkylation of *cis*-1,*k* + 2-diphosphabicyclo[*k.l*.0]-alkanes proceeds readily with standard alkylating agents (iodomethane, benzyl bromide), but the second alkylation is much slower, due to the influence of the adjacent phosphonium centre. In the nitrogen series, it was found that five-membered rings were closed more readily than six-membered (the normal pattern for the cyclisation of carbocyclic rings). Thus cyclisation to form 1,5-diazoniatricyclo[3.3.3]undecane tetrafluoroborate occurred on treatment of 1-(3-hydroxypropyl)-1,5-diazabicyclo[3.3.0]octane bromide with 40% aqueous HBF_4, but more severe reaction conditions involving a combination of a dibromoalkane and silver tetrafluoroborate was required to close six-membered rings.[10] We anticipated similar or greater reactivity for the preparation of the diphosphonium dications, since phosphines are usually at least as good nucleophiles as the corresponding amines. All attempts to prepare **8d** using the dibromoalkane–silver tetrafluoroborate procedure were unsuccessful however, and so we had to consider the use of more powerful alkylating agents. 1,4-Bis(trifluoromethanesulfonyloxy)butane **7b** and 1,5-bis(trifluoromethanesulfonyloxy)pentane **7c** are readily available through reaction of triflic anhydride with THF and tetrahydropyran respectively[14,15] and it was found that the former would react with 1,6-diphosphabicyclo[4.4.0]decane to produce **8d** in about 35% yield if a polar solvent like acetonitrile was used (the reaction did not proceed beyond the first alkylation in dichloromethane). While this yield was just about acceptable, attempts to form lower homologues gave lower yields and in particular the [3.3.3.0] analogue could not be observed even by NMR. At the same time NMR studies suggested that the triflate was being consumed in a parallel reaction through alkylation of the solvent to give a nitrilium ion which did not undergo further cyclisation. Other solvents were therefore sought. Suitable highly polar, but non-nucleophilic, solvents are not numerous; we considered the use of liquid sulfur dioxide, nitromethane, nitrobenzene, and sulfolan and fortunately nitromethane proved quite effective. We also found that yields were significantly improved if the bis-triflate alkylating agents were subjected to chromatography immediately prior to use. In this way the yield of **8d** could be increased to 95%, and the formation of less favourable analogues could be realistically attempted.

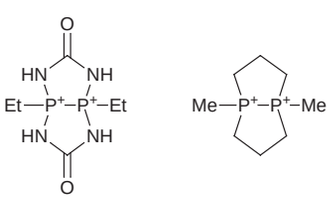
Reaction of 1,6-diphosphabicyclo[4.3.0]nonane **6b** with **7b** in nitromethane led to the formation of **8c** in 55% yield. The dication was obtained as a low-melting point solid and was converted into a hexafluorophosphate for characterisation. Reaction of **7a** with **6c** under similar conditions gave **8c** in an improved 75% yield. 1,3-Bis(trifluoromethanesulfonyloxy)-propane **7a** was prepared by reaction of propane-1,3-diol with trifluoromethanesulfonic anhydride, in the presence of two equivalents of pyridine to remove the trifluoromethanesulfonic acid formed.[15] We find that this bis-triflate is particularly prone to decomposition and it was always prepared and then purified by chromatography immediately before use.

1,6-Diphosphoniatricyclo[4.3.3.0]dodecane bis-triflate **8b** was generated by similar methods. The reaction between 1,6-diphosphabicyclo[4.3.0]nonane **6b** and **7a** in nitromethane was monitored by ^{31}P NMR. After three days the spectrum contained one sharp resonance at δ_P 33.88. The reaction mixture was washed with dichloromethane, and dried under high vacuum to give **8b** as a pale orange oil. All attempts to induce crystallisation of this salt failed, but the identity of the product was confirmed by ^{1}H, ^{13}C and ^{31}P NMR and by FAB mass spectrometery.

1,5-Diphosponiatricyclo[3.3.3.0]undecane bis-triflate **8a** was formed by reaction of **6a** with **7a**. The reaction was monitored by ^{31}P NMR spectroscopy and took approximately two weeks to reach completion at room temperature. Dication **8a** absorbs at δ_P 60.72, and two additional species were present during the reaction, *both* of which slowly formed dication. One of these is presumably the expected monoalkylated diphosphine with a terminal triflate; we suggest that the other is the related compound where the pendant alkyl triflate has alkylated a molecule of solvent. It is known that nitro groups are among the least basic strongly polar groups, the O-alkylated nitronate is likely to be an effective alkylating agent. Early attempts to isolate **8a** from the reaction mixture failed. In addition, analysis of the reaction mixture by FAB mass spectrometry did not give a molecular ion, as it had done for the other related dications. To confirm the identity of **8a** a reaction was performed in CD_3NO_2. As the reaction proceeded the ^{13}C NMR was monitored, and after two weeks a spectrum characteristic of **8a** was obtained [δ_C 26.82 (t, N_{PC} 45), 29.58 (s)]. The problems encountered in the isolation of **8a** can be attributed to its instability towards water (see below). A crude sample was obtained by adding dry dichloromethane to the reaction mixture, and decanting off the solution to leave a pale orange oil, but the material could not be obtained in analytical purity.

It is clear from the above that the reactivity order for cyclisation is quite different for the diphosphines and the hydrazines. We believe that this is due mainly to strain in the cyclisation transition states, related to strain in the products. Whereas the N–N bond is readily accommodated in all the ring systems from [3.3.3.0] to [4.4.4.0], accommodating long P–C and, particularly, P–P bonds in the smaller ring systems causes considerable strain. We have pointed out elsewhere[16] that the introduction of a P–P unit at the 9,10-positions of decalin causes a dramatic shift in the relative strain in *cis*- and *trans*-isomers. Semi-empirical PM3 calculations give the following ΔH_f and P–P distances: **8a** [3.3.3.0] 1675, 2.11; **8b** [4.3.3.0], 1619, 2.13; **8c** [4.4.3.0], 1584, 2.17; **8d**, [4.4.4.0], 1550 kJ mol^{-1}, 2.19 (experimental 2.165 Å). If there were no strain energy changes in this series, the addition of a methylene group should result in a decrease in ΔH_f of 20.7 kJ mol^{-1}, and it is clear that the [3.3.3.0] dication **8a** is predicted to be particularly strained. The calculated P–P distance in **8a** is also unusually small, suggesting a bond in compression. We note that the ^{31}P NMR chemical shifts for the dications vary over a wide range: **8a**, 60.72; **8b**, 33.88; **8c**, 8.84; **8d**, −10.59 ppm, these shifts presumably reflect changes in the bond angles at the phosphorus atoms, although we can offer no detailed interpretation.

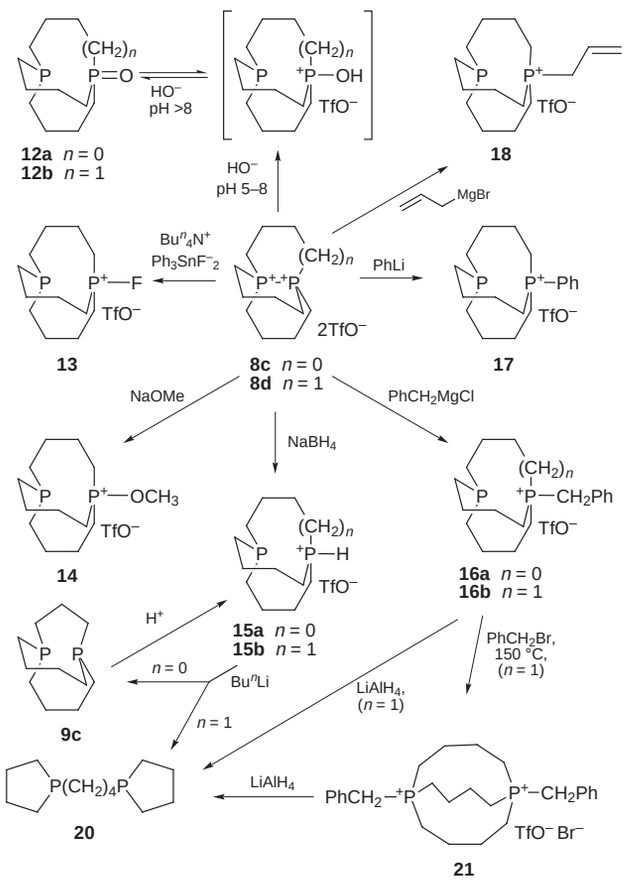
Reactions of propellane 1,*k* + 2-diphosphoniatricyclo[*k.l.m*.0]-alkane bis-triflates. Compounds with two adjacent positively charged phosphorus atoms are very rare. The salt **10** was reported in 1985;[17] in this species some of the positive charge is undoubtedly siphoned off to the nitrogen atoms. We reported[16] that the bicyclic dication **11**, from reaction of **6a** with methyl



10 **11**

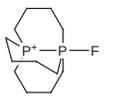
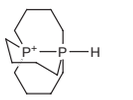
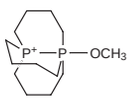
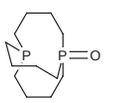
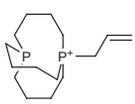
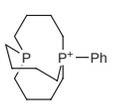
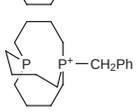
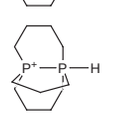
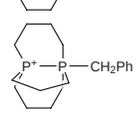
triflate, was instantly hydrolysed by even traces of water. The stability of the tricyclic propellane dications towards hydrolysis by water and hydroxide is strongly dependent on ring size. The most strained propellane dication **8a** is similar to **11** in being instantly hydrolysed by water, whereas **8b**–**8d** are stable in acidic aqueous solutions. Reaction of hydroxide with **8b** is complex, judging from the formation of several peaks in the ^{31}P NMR spectrum, but the two larger dications **8c** and **8d** form single products with hydroxide; these are presumably hydroxide adducts initially which are then further deprotonated by excess hydroxide to monooxides of the diphosphines. Reaction of hydroxide with **8d** is fully reversible; the monooxide **12b** being converted back to **8d** by reaction with strong acid or with methyl triflate (see Scheme 2). We see no evidence in these reactions for a di-cationic addend with Me_2O, for example, as might be expected from the observations of Verkade *et al.*[18] In fact a study of the behaviour of **8d** in D_2O as NaOD was added to the solution suggests that both hydroxide addition and deprotonation are rapidly reversible processes. From pH 2–5.4, the single ^{31}P resonance at δ −10 simply broadens, but above pH 5.4 the resonance splits into two which move apart as the pH is raised, becoming two sharp doublets at δ 53.61 and −44.54 (J 108 Hz) above pH 8.5, corresponding to **12b**. At no point in this sequence do the observed chemical shifts correspond very closely to the methoxide adduct **14** (see below), so we presume that the hydroxide adduct disproportionates extensively to **8d** and **12b**. Preliminary results for reaction of **8c** with hydroxide suggest that hydroxide addition is complete before deprotonation to give phosphine oxides begins, but the latter process is significantly more complex than for **8d**; this work will be reported elsewhere. As described in our preliminary communication, **8d** reacts with suitable nucleophiles to give fluoride **13**, methoxide **14** and hydride **15** adducts (Scheme 2); preparative details are given in the Experimental section. We also find that **8d** reacts with Grignard and organolithium reagents, to give products **16**–**18** in which one alkyl group has been added to a phosphorus atom (Scheme 2). The ^{31}P NMR data for these adducts all show significant P–P coupling, ranging from 46 to 249 Hz (Table 1). These mono-cationic adducts are related to the series of cations, *e.g.* **2**, prepared by Verkade *et al.* by addition of electrophiles to phosphatranes **19**. Verkade's group have shown that there is wide variation in N···P distances in their ions, and it is tempting to associate larger values of J_{PP} in our adducts with tighter P–P bonding. However, we have now obtained X-ray crystal structures of three of these adducts, and it is already clear that there is no simple relationship between J_{PP} in solution and P–P distance. We will discuss the nature of the P–P interactions in these interesting compounds when we have accumulated more structural data.

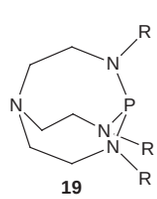
The [4.4.3.0]dication salt **8c** reacts with sodium borohydride to give **15a**, and with benzylmagnesium chloride to give **16b**, both adducts show significantly larger J_{PP} values than the corresponding adducts from **8d**.



Scheme 2

Table 1 ^{31}P NMR data of adducts of tricyclic dications

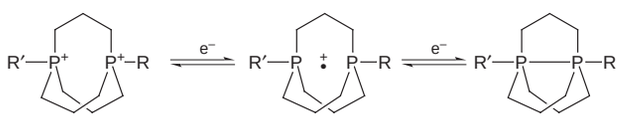
Compound	Compound no.	δ_P(P*P*Nu)	δ_P(*P*PNu)	J_{PP} (Hz)
	**13**	−63.21	−7.82	198
	**15b**	−83.08	−12.33	178
	**14**	−30.23	−16.37	139
	**12b**	−44.54	+53.61	108
	**18**	−27.18	−17.87	67
	**17**	−25.47	−19.05	46
	**16b**	−27.86	−12.35	46
	**15a**	−79.95	−32.73	249
	**16a**	−42.92	−23.81	139



19

Preparations of 1,*k* + 2-diphosphabicyclo[*k.l.m*]alkanes from 1,*k* + 2-diphosphoniatricyclo[*k.l.m*.0]alkane bis-triflates

We now turn to our attempts to prepare 1,*k* + 2-diphosphabicyclo[*k.l.m*]alkanes **9** (Scheme 1) from the dication salts **8**. When we began this work, we imagined that this would be a simple matter of electron-transfer reduction, hopefully *via* stable radical cations, as is observed in the nitrogen series. To our amazement, radical cations derived by reduction of **8** are extremely short-lived. Electrochemical reduction of **8d** is irreversible, even at −80 °C, and pulse radiolysis suggests that the radical cation cannot have a lifetime of greater than about 1 μs at ambient temperature. This is in astonishing contrast to the indefinite stability of the corresponding nitrogen species. Details of our investigation into this radical cation will be discussed elsewhere, suffice it to say that electron-transfer reduction does not offer a practical route to the diphosphines **9**. We have also briefly examined the possibility of a different set of electron transfer equilibria involving bridgehead diphosphorus species. Bicyclic dications, such as **23a** (see below for preparative details), are potentially reducible by two one-electron steps to neutral tricyclic species (Scheme 3). In practice, **23a** was



Scheme 3

not reduced at potentials attainable in acetonitrile. This could be due to the reluctance of methyl groups to adopt apical positions on trigonal bipyramidal phosphorus, and we intend exploring this type of reduction with dications containing more apicophilic groups.

The hydride adducts **15a** and **15b** are formally simply protonated salts of **9**, and we fully expected that deprotonation would yield the diphosphines. As reported in our preliminary communication, compound **15b** was recovered unchanged from treatment with one of the strongest known proton sponges 2,7-dimethoxy-1,8-bis(dimethylamino)naphthalene ($pK_a \approx 16.1$).[19] This is not too surprising, as Verkade has shown that **2**, X = H has $pK_a > 16$. When we treated **15b** with Bu^{n}Li in THF, a remarkable rearrangement took place and 1,4-bis(1-phospholan-1-yl)butane, **20** (δ_P −27.3), was obtained in 55% yield. Independent synthesis from 1,4-diphosphinobutane confirmed the structure of this product (see Experimental section). In view of the success with **15a** (see below), we are currently examining this reaction using a wider variety of strong bases in the hope of finding conditions which yield some **9d**.

We find that the reaction of the next smaller homologue **15a** with Bu^{n}Li in THF gives a product which shows a single ^{31}P NMR signal at δ_P −21.06, and which is not (by direct comparison) the corresponding rearrangement product 1,3-bis-(1-phospholan-1-yl)propane. The product is indeed the hoped for **9c**, presumably the *out*,*out*-isomer, since it is converted back to **15a** when treated with acid. So far we have been unable to obtain structural data on **9c**, but it can be converted to a disulfide with apparently normal properties. Since **15a** shows a strong P–P coupling, it must surely be the isomer with the unprotonated phosphorus atom inside, whatever the precise nature of the P···P interaction. Therefore the deprotonation–reprotonation reactions must proceed with inversion at the phosphorus atom which is not formally involved. Considering the high barrier normally associated with phosphorus inversion, this is a surprising observation, and we are currently examining these reactions in more detail.

Various methods have been developed for the reduction of phosphonium salts to phosphines. We hoped to utilise such a reaction in order to form the medium-ring bicyclic diphosphine **9d** from other adducts of **8d**. Gough and Trippett[20] reported the reductive removal of phenyl groups from a range of Ph_3P^+R salts with $LiAlH_4$. Using similar conditions to those described, the phenyl adduct **17** was treated with a commercial solution of $LiAlH_4$ in THF. The reaction mixture was sonicated and monitored by ^{31}P NMR, which showed that at least three different products were present, as five lines were visible ranging from δ_P −35 to δ_P −5. As debenzylation of a much wider range of phosphonium salts had been reported we turned our attention to the reduction of benzyl adduct **16b**. Bailey and Buckler[21] studied a range of methods for the removal of benzyl groups from a series of phosphonium salts and found that $LiAlH_4$ was the preferred reagent; other methods which have been reported include electrolysis[22,23] and potassium napthalenide.[23] The reaction of **16b** with $LiAlH_4$ was monitored by ^{31}P NMR spectroscopy, and after the appearance and disappearance of five separate resonances, a single line remained at δ_P −26.51. The reaction gave a waxy white solid, and the ^{13}C NMR confirmed this was the same rearrangement product **20** obtained from the deprotonation of the hydride adduct **15b**. We also prepared the dibenzyl dication salt **21** by reaction of **16b** with benzyl bromide at 150 °C (another reaction which must involve inversion at phosphorus) and examined its reductive debenzylation, but **20** was again the only product. The reaction of hydride with benzylphosphonium salts is thought[21] to proceed by S_N2 attack by hydride on the benzyl carbon atom ejecting the neutral phosphine, but we can only speculate on the course of these reactions which lead to rearrangement to **20**; it may be that deprotonation of α-methylene groups is involved, but we have yet to conduct any labelling experiments. It is worth noting that attempts to prepare bicyclo[4.4.4]tetradeca-1,6-diene, using McMurry Ti^0 coupling led to 1,4-bis(cyclopent-1-enyl)butane,[24] showing the same basic skeletal rearrangement. Although these reactions must have very different mechanisms, the relief of strain in the bicyclo[4.4.4]tetradecane skeleton is surely a common factor.

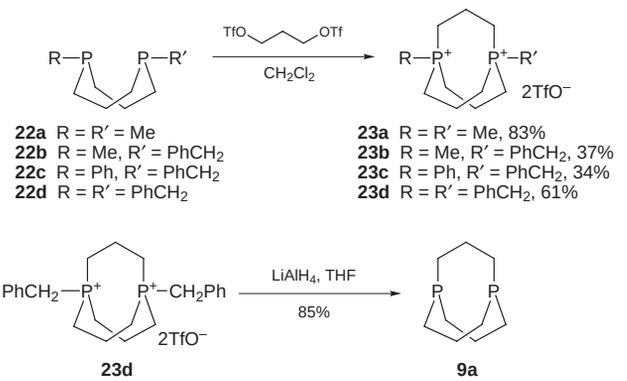
Cyclisation route to 1,5-diphosphabicyclo[3.3.3]undecane

A few examples of bicyclic diphosphines containing common-sized rings have been prepared by direct cyclisation procedures. Hinton and Mann[25] reported that reaction of the 1,4-dibenzyl-1,4-diphosphacyclohexane with 1,2-dibromoethane led to the bicyclic dication salt, which was de-benzylated to 1,4-diphosphabicyclo[2.2.2]octane with $LiAlH_4$. Employing a similar procedure Gallagher *et al.*[26] reported the synthesis of 1,5-diphenyl-1,5-diphosphonia[3.2.2]nonane dibromide, although removal of the phenyl groups from this compound was not discussed. In addition, 1,5-diphosphabicyclo[3.3.1]nonane has been synthesised by radical cyclisation of 1,3-diallyl-1,3-diphosphapropane.[27]

These direct ring-closure routes generally fail to work for compounds composed entirely of medium-rings, due to the strain penalty associated with such systems. This is emphasised by the radical-induced cyclisation of allylphosphine, which was initially reported to give 1,5-diphosphabicyclo[3.3.3]-undecane,[28] but actually forms 1,5-diphosphabicyclo[3.3.0]-octane. Attempts to prepare derivatives of 1,5-diazabicyclo-[3.3.3]undecane by direct ring closure methods generally give very low yields, at best. Thus naphtho-[1,8-*bc*]-1,5-diazabicyclo-[3.3.3]undecane was obtained in yields of up to 5% by reaction of 1,8-diaminonaphthalene with 1,3-dibromopropane,[29] and 3,7,10-trimethylene-1,5-diazabicyclo[3.3.3]undecane was obtained from 1-amino-2-aminomethylpropene and 1-iodo-2-iodomethylpropane in 32% yield.[30] This latter example may be a rather special case, and attempts to prepare 1,5-diazabicyclo-[3.3.3]undecane itself from 1,5-diazacyclooctane and 1,3-dibromopropane or the corresponding bis-triflate led to yields of below 1%.[31]

In spite of these discouraging precedents, we investigated direct ring-closure routes to 1,5-diphosphabicyclo[3.3.3]undecane **9a**. Initially experiments were conducted with 1,5-dimethyl-1,5-

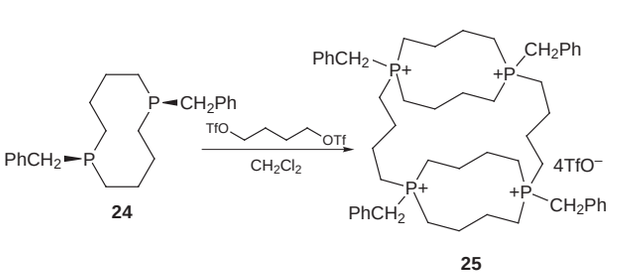
diphosphacyclooctane **22a**. 1,3-Diiodopropane and **22a** were slowly added simultaneously to a volume of dichloromethane but this only led to the isolation of an insoluble sticky white solid which is presumably polymeric in nature. High dilution procedures are only effective if the chemical reactions are fast compared with the rate of addition, and the above procedure was therefore repeated with highly reactive $CH_2(CH_2OTf)_2$ in place of 1,3-diiodopropane. A white precipitate formed instantly in the reaction flask and, after stirring for one hour, this was filtered off. The ^{31}P NMR spectrum showed one resonance at δ_P 35.93, consistent with a phosphonium salt. The ^{13}C NMR spectrum contained two doublets and a triplet which strongly suggested the formation of the medium-ring bicyclic dication **23a** (Scheme 4). The structure was further confirmed



Scheme 4

by FAB mass spectrometry and elemental analysis. The formation of **23a** using this procedure occurs with remarkable ease, giving yields of up to 83%. A series of compounds **23b–d** were prepared by similar reactions (see Experimental section). The dibenzyl compound **23d**, which might be de-alkylated to reveal the 1,5-diphosphabicyclo[3.3.3]undecane **9a**, initially gave very poor yields, but this was improved to an acceptable 61% by performing the reaction at reflux and the use of a mechanical syringe pump. The X-ray crystal structure determination of **23d** has been reported.[7] Dication salt **23d** is surprisingly resistant to hydrolysis, being recovered unchanged after treatment with aqueous sodium hydroxide at 100 °C for three days. Hydrolysis of phosphonium centres is thought to proceed through a pentavalent phosphorus atom,[32] and the stability of **23d** to base hydrolysis may be a result of the strain penalty involved with having a pentavalent phosphorus atom at the bridgehead of the bicyclic system.

Although the preparation of **23** was a pleasant surprise, attempts to extend this ring closure procedure to larger rings failed. When the ten-membered ring diphosphine *cis*-1,6-dibenzyl-1,6-diphosphacyclodecane **24** is reacted with $(CH_2CH_2OTf)_2$ under similar conditions, 1,6-dibenzyl-1,6-diphosponiabicyclo[4.4.4]undecane bis-triflate **21** is not obtained. The major product (Scheme 5) is 1,6,11,16-tetrabenzyl-1,6,11,16-tetraphosphoniatricyclo[14.4.4.4^{6,11}]octacosane tetrakis(trifluoromethanesulfonate) **25**, a potential precursor of an intriguing macropolycyclic tetraphosphine,[7] whose reactions



Scheme 5

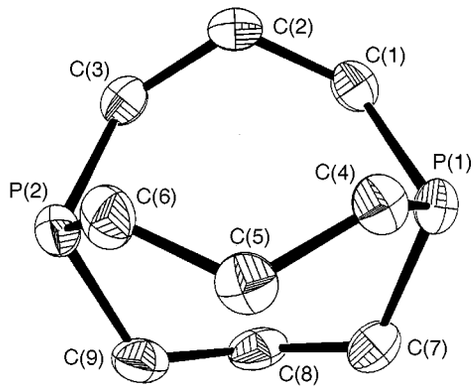


Fig. 1 Molecular structure of 1,5-diphosphabicyclo[3.3.3]undecane **9a** showing atom labelling, displacement ellipsoids are drawn to enclose 50% probability density. All hydrogen atoms are omitted for clarity.

we intend to examine. We also found that reaction of 1,5-dimethyl-1,5-diphosphacyclononane with $CH_2(CH_2OTf)_2$ under the conditions which gave **23d** in 61% yield, only led to oligomeric products. Reaction of **23d** with $LiAlH_4$ led to the isolation of a waxy solid, whose ^{31}P NMR spectrum contained a single sharp resonance at −30.11 ppm. The ^{13}C NMR spectrum of the product contained two resonances which were consistent with the desired bicyclic diphosphine **9a** [δ_C 19.02 (t, $^2J_{PC}$ 4), 19.82 (d, $^1J_{PC}$ 21)]. In addition, high-resolution mass spectrometry gave $C_9H_{18}P_2$ as the composition of the molecular ion. This evidence strongly suggests that the desired medium-ring diphosphine **9a** had been formed.

Properties of 1,5-diphosphabicyclo[3.3.3]undecane

1,5-Diphosphabicyclo[3.3.3]undecane **9a** is a waxy solid which melts at approximately 20 °C. It reacts readily with atmospheric oxygen to form a dioxide, and also with excess benzyl bromide to return the dibenzyl dication salt **23d**. Crystals of suitable quality for an X-ray crystal structure determination were obtained by slow sublimation. A small sample of **9a** was placed in an evacuated Schlenk tube (0.1 Torr). The tube was placed in a room held at 4 °C and the base of the tube was heated at approximately 40 °C. Over a period of three weeks suitable crystals formed on the upper region of the tube. The X-ray crystal structure of **9a** is shown in Fig. 1; the diphosphine adopts the expected *out*,*out*-conformation similar to that of manxane,[33] with approximate C_{3h} symmetry. Bond lengths, angles and torsion angles for **9a** are given in Table 2. The PC_3 units are eclipsed with CP···PC torsions close to zero, in the range −0.4(2)–1.6(2)°, as required for C_{3h}. The P···P distance is 4.073(1) Å, which is significantly greater than in the dibenzyl dication salt **23d** and the C–P–C angles are smaller (106 *vs.* 110°) than for **23d** although still larger than normal for phosphines (C–P–C angles are typically *ca.* 99° in trialkylphosphines). In the corresponding nitrogen compounds, the reverse is true. Thus 1,5-diazabicyclo[3.3.3]undecane **3** has C–N–C angles close to 120°, which decrease on quaternisation. Undoubtedly, the ring system seeks to impose planarity, but the preference of phosphines for small C–P–C angles is still apparent, and the resulting strain is reflected in the large values of the average P–C–C and C–C–C angles in **9a** (123.6 and 118.2° respectively). In contrast the bond lengths show little deviation from unstrained values (mean P–C 1.850 Å, mean C–C 1.529 Å).

The photoelectron spectrum of 1,5-diphosphabicyclo-[3.3.3]undecane **9a** is shown in Fig. 2. The PE spectra of two monocyclic medium-ring diphosphines, 1,5-dimethyl-1,5-diphosphacyclooctane and 1,6-dimethyl-1,6-diphosphacyclodecane show very little, or no, splitting between the bands associated with the lone pair orbitals.[9] The strong splitting of the first two bands in the PE spectrum of 1,5-diphosphabicyclo-[3.3.3]undecane therefore deserves comment. To understand

Table 2 Selected bond lengths (Å), angles and torsion angles (°) for **9a**

P(1)–C(4)	1.849(3)	C(1)–C(2)	1.525(4)
P(1)–C(1)	1.851(3)	C(2)–C(3)	1.528(4)
P(1)–C(7)	1.856(3)	C(4)–C(5)	1.534(4)
P(1)–P(2)	4.073(1)	C(5)–C(6)	1.536(4)
P(2)–C(9)	1.847(3)	C(7)–C(8)	1.527(4)
P(2)–C(3)	1.848(3)	C(8)–C(9)	1.533(4)
P(2)–C(6)	1.851(3)		
C(4)–P(1)–C(1)	106.4(2)	C(2)–C(3)–P(2)	123.0(2)
C(4)–P(1)–C(7)	105.1(2)	C(5)–C(4)–P(1)	123.7(2)
C(1)–P(1)–C(7)	106.0(2)	C(4)–C(5)–C(6)	118.1(2)
C(9)–P(2)–C(3)	106.4(2)	C(5)–C(6)–P(2)	122.7(2)
C(9)–P(2)–C(6)	105.4(2)	C(8)–C(7)–P(1)	123.0(2)
C(3)–P(2)–C(6)	105.0(2)	C(7)–C(8)–C(9)	118.5(3)
C(2)–C(1)–P(1)	123.2(2)	C(8)–C(9)–P(2)	124.1(2)
C(1)–C(2)–C(3)	117.9(2)		
C(4)–P(1)–P(2)–C(9)	−118.31(2)	C(6)–P(2)–C(3)–C(2)	23.3(3)
C(1)–P(1)–P(2)–C(9)	120.67(2)	C(1)–P(1)–C(4)–C(5)	87.0(3)
C(7)–P(1)–P(2)–C(9)	0.33(2)	C(7)–P(1)–C(4)–C(5)	−25.1(3)
C(4)–P(1)–P(2)–C(3)	120.6(2)	P(1)–C(4)–C(5)–C(6)	−78.1(3)
C(1)–P(1)–P(2)–C(3)	−0.4(2)	C(4)–C(5)–C(6)–P(2)	80.5(3)
C(7)–P(1)–P(2)–C(3)	−120.8(2)	C(9)–P(2)–C(6)–C(5)	21.1(3)
C(4)–P(1)–P(2)–C(6)	1.6(2)	C(3)–P(2)–C(6)–C(5)	−91.0(3)
C(1)–P(1)–P(2)–C(6)	−119.5(2)	C(4)–P(1)–C(7)–C(8)	89.4(3)
C(7)–P(1)–P(2)–C(6)	120.2(2)	C(1)–P(1)–C(7)–C(8)	−23.0(3)
C(4)–P(1)–C(1)–C(2)	−21.3(3)	P(1)–C(7)–C(8)–C(9)	−77.7(4)
C(7)–P(1)–C(1)–C(2)	90.1(3)	C(7)–C(8)–C(9)–P(2)	79.1(4)
P(1)–C(1)–C(2)–C(3)	−80.7(3)	C(3)–P(2)–C(9)–C(8)	21.9(3)
C(1)–C(2)–C(3)–P(2)	79.6(3)	C(6)–P(2)–C(9)–C(8)	−89.4(3)
C(9)–P(2)–C(3)–C(2)	−88.1(3)		

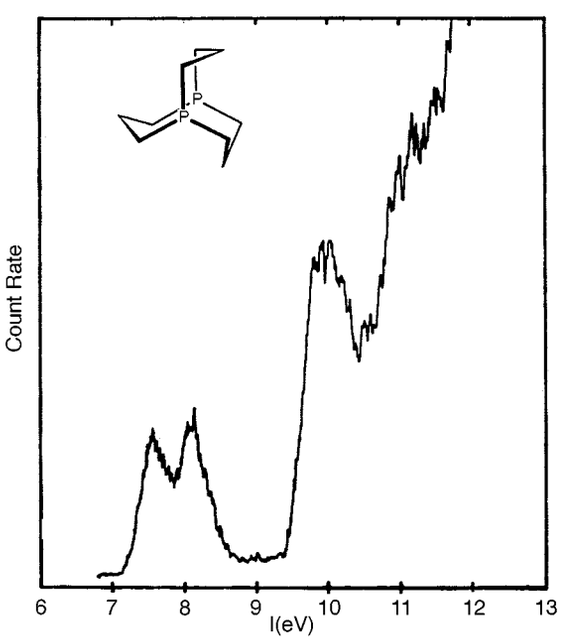


Fig. 2 He(I) photoelectron spectrum of 1,5-diphosphabicyclo[3.3.3]-undecane

this we have carried out *ab initio* calculations applying the Hartree–Fock self consistent field (HF-SCF) procedure using a 6-31G* basis set.[34] A geometry optimisation of 1,5-diphosphabicyclo[3.3.3]undecane was carried out assuming a C_{3h} point group. The through-space and through-bond interactions were calculated according to the Heilbronner–Schmelzer procedure,[35] as later modified by Imamura and Ohsaku.[36] It is based on the Fock-matrix in a localised basis set. We used Weinhold's natural bond orbitals, NBOs, as a starting point for our calculation.[37] These localised orbitals incorporate well-known features like hybridisation, and are therefore close to chemical intuition.

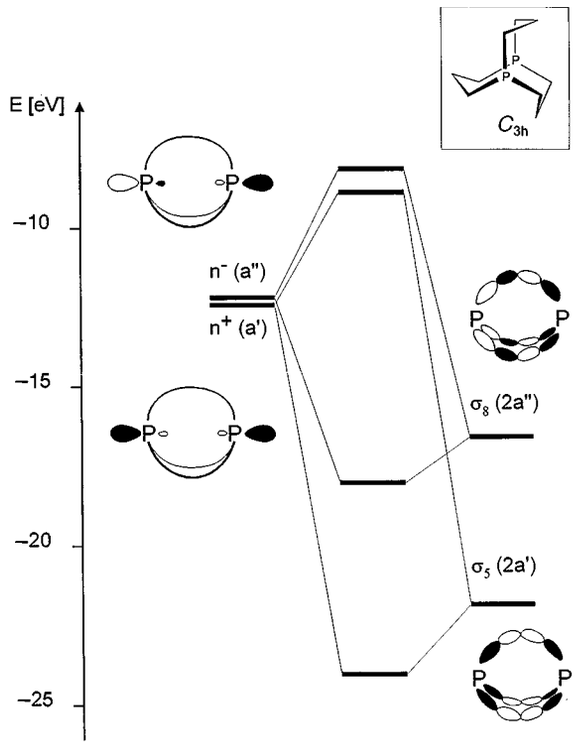


Fig. 3 Orbital interaction diagram for the a′ and a″ orbitals of 1,5-diphosphabicyclo[3.3.3]undecane

The HF optimised geometry of 1,5-diphosphabicyclo[3.3.3]-undecane is in good agreement with the values of the X-ray structure determination. The transannular P–P distance is calculated (measured) to be 4.070 [4.0729(11)] Å. The energy of the HOMO (−8.09 eV) is 0.48 eV apart from the HOMO-1 (−8.57 eV). The calculated splitting corresponds well to the recorded difference of the first two bands (0.59 eV) if we adopt Koopmans' theorem.[38]

The interaction of the lone pairs located at the two phosphorus atoms, is caused by a strong n/σ mixing with the orbitals of the bicyclic cage. The through-space effect between the lone pairs is minor. This could have been expected from the large distance, 4 Å, between P(1) and P(2). However, a second point must be taken into consideration: the NBO-analyses reveal high s-character for the lone pair, $sp^{1.3}$. This is a common feature on going from 2nd row elements to 3rd row ones. As a result, the lobes of the lone pairs point away from each other.

Consequently, the overlap between the orbitals is very small, and therefore the energetical split between the antibonding $n^-(a'')$- and the bonding $n^+(a')$-combination is negligible. Both linear combinations are shown on the left-hand side of Fig. 3. The $n^-(a'')$-orbital is only 0.04 eV higher in energy than its bonding counterpart at −12.12 eV. As mentioned above, interaction with the σ-orbitals of the bicyclo[3.3.3]undecane system is a significant feature in 1,5-diphosphabicyclo[3.3.3]undecane. We derive these cage-orbitals as a linear combination of the 6 σ-C–P-NBOs and the 6 σ-C–C-NBOs. This leads to 12 symmetry adapted precanonical molecular orbitals, PCMOs, σ_1 to σ_{12}. Group theory shows that they belong to the following irreducible representations of the C_{3h} point group:

$$2a' + 2e' + 2a'' + 2e''$$

Note that the n^+ and the n^- orbitals belong to the one-dimensional representations (a′ and a″). Therefore the e′- and e″-type degenerate orbitals need not to be considered in the through-bond coupling. Further simplification can be achieved if perturbational theory arguments are taken into account, *i.e.* that only σ-orbitals which are energetically close to the lone pairs can cause a strong interaction.

There are two σ-orbitals which match these requirements: first, the PCMO $\sigma_5(2a')$ at −21.8 eV and, second, $\sigma_8(2a'')$ at −16.5 eV. Both are shown at the right hand side of the interaction diagram (Fig. 3). The smaller energy gap between the $\sigma_8(2a'')$ and $n^-(a'')$-PCMO leads to a stronger antibonding interaction, compared to the two a′-type orbitals. As a result, the $\sigma_8(2a'')$–$n^-(a'')$-combination becomes the HOMO, whereas the HOMO-1 is dominated by the $\sigma_5(2a')$–$n^+(a')$-combination. The stronger n/σ interaction for the HOMO is also supplied by its percentile composition with respect to the lone pairs. In the case of the HOMO, the lone pair contributed only amounts up to 71%, while the HOMO-1 has 73% lone-pair character.

In summary, the interactions in 1,5-diphosphabicyclo-[3.3.3]undecane can therefore be readily understood in terms of the through-space/through-bond concept. The situation is entirely different in the corresponding diamine, 1,5-diazabicyclo[3.3.3]undecane, where the split between the first two ionisation energies is almost three times larger (ΔI = 1.50 eV *vs.* 0.56 eV in the diphosphine).[39,40] This difference is mainly due to the fact that the nitrogen atoms are strongly flattened in the diamine, so that the lone pairs, which have high p character, interact strongly through space. A more detailed analysis, based on 6-31G* calculation of the diamine, shows that this is enhanced by considerable through-bond interaction, which had earlier been assumed not to be important.[39,40] The calculations suggest that through-space interaction contributes about 0.7 eV, and the through-bond effect 0.8 eV. In the diphosphine, the phosphorus atoms are too far away for a significant through-space effect; the overlap between the lone pairs is too small. However, the bicyclic cage acts as a relay system (through-bond effect) which is mediated by two orbitals, the PCMOs $\sigma_5(2a')$ and $\sigma_8(2a'')$. They strongly influence the lone pairs because they have the proper symmetry and are high enough in energy.

Conclusions

Propellane dications **8a**–**d** with phosphonium bridgeheads can be prepared by cycloalkylation, but are very different from the corresponding nitrogen systems, and their properties are strongly dependent on ring size. Electrochemical reduction of **8d** leads to a very short-lived radical cation, unlike the corresponding nitrogen system. Dications like **8d** add a variety of nucleophiles; the structure and reactivity of the adducts formed are interesting and will be the subject of further studies. Two bicyclic diphosphines, **9a** and **9c**, have been prepared (by conceptually different routes), and the structure, photoelectron spectrum, and other properties of **9a** have been examined. In closing, we note that although substantial progress has now been made in the synthesis of these compounds, some interesting ring systems, such as the [5.5.5] system which might show *in*,*in*-geometry remain out of reach.

Experimental

General procedures

Solvents and reagents used in this work were purified according to standard literature techniques 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 uncorrected. 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-Diphosphoniatricyclo[*n.m.l*.0]alkane bis(trifluoromethanesulfonates) and precursors

1,3-Bis(trifluoromethanesulfonyloxy)propane 7a. Following the literature method,[15] a solution of propane-1,3-diol (1.02 g, 13.4 mmol) and pyridine (2.12 g, 26.8 mmol) in CH_2Cl_2 (10 cm^3) was added dropwise to a solution of trifluoromethanesulfonic anhydride (4.5 cm^3, 27 mmol) in CH_2Cl_2 (40 cm^3) at −78 °C. After warming to room temperature the reaction was stirred for one hour, resulting in a pink solution containing a white precipitate. The reaction mixture was washed with water (3 × 5 cm^3), dried ($MgSO_4$) and purified by filtration through silica (15 g). Removal of the solvent *in vacuo* gave the title compound, an unstable clear oil (3.49 g, 79%); $\delta_H(CDCl_3)$ 2.35 (2 H, quintet, $^3J_{HH}$ 6, 2-CH_2), 4.66 (4 H, t, $^3J_{HH}$ 6, 1-CH_2, 3-CH_2); δ_C 29.25 (1 C, s, C-2), 71.29 (2 C, s, C-1, C-3), 118.54 (2 C, q, $^1J_{FC}$ 313, *C*F$_3$).

1,4-Bis(trifluoromethanesulfonyloxy)butane 7b. Following the literature method,[15] a solution of trifluoromethanesulfonic anhydride (5.5 cm^3, 33 mmol) in CH_2Cl_2 (80 cm^3), at −78 °C, was treated with a solution of THF (2.35 g, 32.7 mmol) in CH_2Cl_2 (20 cm^3). The same procedure as described above was employed to give a white solid (7.31 g, 63%); $\delta_H(CDCl_3)$ 2.00 (4 H, s, 2-CH_2, 3-CH_2), 4.59 (4 H, s, 1-CH_2, 4-CH_2); δ_C 25.36 (2 C, s, C-2, C-3), 75.24 (2 C, s, C-1, C-4), 118.53 (2 C, q, $^1J_{FC}$ 315, *C*F$_3$).

1,5-Bis(trifluoromethanesulfonyloxy)pentane 7c. Following the literature method,[15] a solution of trifluoromethanesulfonic anhydride (5.0 cm^3, 30 mmol) in CH_2Cl_2 (80 cm^3), at −78 °C, was treated with a solution of tetrahydropyran (2.56 g, 30 mmol) in CH_2Cl_2 (20 cm^3). The same procedure as described above was employed to give the title compound, a clear oil (6.84 g, 62%); $\delta_H(CDCl_3)$ 1.5–1.7 (2 H, m, 3-CH_2), 1.8–1.9 (4 H, m, 2-CH_2, 4-CH_2), 4.53 (4 H, t, $^3J_{HH}$ 6, 1-CH_2, 5-CH_2); δ_C 21.08 (1 C, s, C-3), 28.50 (2 C, s, C-2, C-4), 76.73 (2 C, s, C-1, C-5), 118.56 (2 C, q, $^1J_{FC}$ 317, *C*F$_3$).

1,5-Diphosphoniatricyclo[3.3.3.0]undecane bis(trifluoromethanesulfonate) 8a. A solution of 1,3-bis(trifluoromethanesulfonyloxy)propane (230 mg, 0.68 mmol) in deuterated nitromethane (1 cm^3) was treated with a solution of 1,5-diphosphabicyclo[3.3.0]octane (100 mg, 0.68 mmol) in deuterated nitromethane (1 cm^3). The reaction was monitored by both ^{31}P and ^{31}C NMR and was judged to be complete after two weeks; $\delta_C(CD_3NO_2)$ 26.82 (6 C, t, N_{PC} 45, C-2, C-4, C-6, C-8, C-9, C-11), 29.58 (6 C, s, C-3, C-7, C-10); δ_P 60.72.

1,6-Diphosphoniatricyclo[4.3.3.0]dodecanediium bis(trifluoromethanesulfonate) 8b. A solution of 1,3-bis(trifluoromethanesulfonyloxy)propane (1.02 g, 3.00 mmol) in nitromethane (5 cm^3) was treated with a solution of 1,6-diphosphabicyclo-[4.3.0]nonane (368 mg, 2.30 mmol) in nitromethane (2 cm^3). After stirring for three days at room temperature the majority of the solvent was removed *in vacuo*, and the product was precipitated by the addition of CH_2Cl_2 to yield an orange oil (874 mg, 76%); $\delta_H(CD_3CN)$ 2.2–2.8 (8 H, m), 2.97 (12 H, m); δ_C 20.88 (2 C, t, N_{PC} 17, C-3, C-4), 22.32 (2 C, X part of an ABX system, N_{PC} 32, C-2, C-5), 26.47 (2 C, s, C-8, C-11),

27.42 (4 C, X part of an ABX system, N_{PC} 47, C-7, C-9, C-10, C-12); δ_P 33.88; *m/z* (FAB$^+$) 351 ($M^+ - CF_3SO_3$, 32%), 201 ($M^+ + 1 - 2CF_3SO_3$, 37). Attempts to crystallise the product failed, and therefore an accurate elemental analysis has not been obtained.

1,6-Diphosphoniatricyclo[4.4.3.0]tridecane bis(trifluoromethanesulfonate) 8c and bis(hexafluorophosphate). A solution of 1,3-bis(trifluoromethanesulfonyloxy)propane (2.31 g, 6.79 mmol) in nitromethane (10 cm^3) was treated with a solution of 1,6-diphosphabicyclo[4.4.0]decane (1.14 g, 6.55 mmol) in nitromethane (5 cm^3). The same procedure as described above yielded a pale yellow oil (2.51 g, 75%); $\delta_H(CD_3CN)$ 1.6–2.0 (10 H, m), 1.8–3.0 (12 H, m); δ_C 19.99 (4 C, s, C-3, C-4, C-8, C-9), 20.06 (4 C, X part of an ABX system, N_{PC} 32, C-2, C-5, C-7, C-10), 24.37 (1 C, t, $^2J_{PC}$ 3, C-12), 25.03 (2 C, t, N_{PC} 47, C-11, C-13); δ_P 8.84; *m/z* (FAB$^+$) 365 ($M^+ - CF_3SO_3$, 31%), 215 ($M^+ + 1 - 2CF_3SO_3$, 100). Attempts to crystallise the product failed, and therefore a satisfactory elemental analysis has not been obtained. The bis(hexafluorophosphate) salt was prepared by adding ammonium hexafluorophosphate (273 mg, 1.67 mmol) to a solution of 1,6-diphosphonia[4.4.3.0]tetradecane bis(trifluoromethanesulfonate) (344 mg, 0.67 mmol) in water (3 cm^3). The white precipitate formed was collected by filtration *in vacuo*, and washed with cold water. The filtered solid was then recrystallised from acetonitrile–diethyl ether to yield colourless crystals (161 mg, 47%), mp >230 °C (Found: C, 26.37; H, 4.58. $C_{11}H_{22}P_4F_6$ requires C, 26.08; H, 4.38%).

1,6-Diphosphoniatricyclo[4.4.4.0]tetradecane bis(trifluoromethanesulfonate) 8d, bis(hexafluorophosphate) and bis(tetrafluoroborate). A solution of 1,4-bis(trifluoromethanesulfonyloxy)butane (2.01 g, 5.68 mmol) in nitromethane (10 cm^3) was treated with a solution of 1,6-diphosphabicyclo[4.4.0]decane (900 mg, 5.17 mmol) in nitromethane (5 cm^3). A similar procedure as described above was employed, and after 20 hours all volatiles were removed *in vacuo*. The resulting residue was recrystallised from acetonitrile and CH_2Cl_2 to give a hygroscopic white solid (2.60 g, 95%) mp >300 °C (Found: C, 31.7; H, 4.9. $C_{14}H_{24}F_6O_6P_2S_2$ requires C, 31.8; H, 4.6%); $\delta_H(CD_3CN)$ 2.18 (12 H, m), 2.91 (12 H, m); δ_C 17.16 (6 C, t, N_{PC} 32, C-2, C-5, C-7, C-10, C-11, C-14), 19.99 (6 C, s, C-3, C-4, C-8, C-9, C-12, C-13); δ_P −10.59. Slow crystallization of a small sample, using a diffusion tank set-up with acetonitrile and dichloromethane at 0 °C, produced colourless crystals of sufficient quality to allow an X-ray structural analysis of the product to be performed. The bis(hexafluorophosphate) salt was prepared by adding ammonium hexafluorophosphate (55 mg, 0.34 mmol) to a solution of 1,6-diphosphonia[4.4.4.0]tetradecane bis(trifluoromethanesulfonate) (72 mg, 0.14 mmol) in water (0.5 cm^3). The white precipitate formed was collected by filtration *in vacuo*, and washed with cold water. The filtered solid was then recrystallised from acetonitrile–diethyl ether to yield colourless crystals (52 mg, 74%), mp 224–226 °C (Found: C, 27.62; H, 4.29. $C_{12}H_{24}P_4F_{12}$ requires C, 27.71; H, 4.65%). The bis(tetrafluoroborate) salt was prepared by adding a solution of sodium tetrafluoroborate (180 mg, 1.6 mmol) in methanol (1.5 cm^3) to a solution of 1,6-diphosphonia[4.4.4.0]tetradecane bis(trifluoromethanesulfonate) (397 mg, 0.75 mmol) in methanol (2 cm^3). The white precipitate formed was collected by filtration *in vacuo*, and washed with cold methanol to yield a white solid (crude yield 235 mg, 78%). Recrystallisation from acetonitrile–diethyl ether failed to remove residual sodium tetrafluoroborate (2–5%).

Derivatives of 1,*n* + 2-diphosphoniatricyclo[*n.m.l*.0]alkane bis(trifluoromethanesulfonates)

1,6-Diphosphabicyclo[4.4.4]tetradecane-1-oxide 12b. A stirred solution of 1,6-diphosphoniatricyclo[4.4.4.0]tetradecane bis(trifluoromethanesulfonate) (106 mg, 0.20 mmol) in water (5 cm^3) was treated with an excess of aqueous sodium hydroxide (2 mol dm^{-3}, 0.5 cm^3, 1 mmol). All volatiles were removed *in vacuo* to leave a solid residue, which was extracted with acetonitrile (2 × 5 cm^3), filtered and evaporated to dryness to give the title compound contaminated with sodium trifluoromethanesulfonate mp 105–110 °C [Found (EI): 246.1284. $C_{12}H_{24}OP_2$ requires 246.1302]; $\delta_H(CD_3CN)$ 1.57 (6 H, m), 1.71 (6 H, m), 1.90 (6 H, m), 2.35 (6 H, m); δ_C 25.17 (3 C, d, $^2J_{PC}$ 8, C-4, C-8, C-13), 25.80 (3 C, br, C-5, C-7, C-14), 28.45 (3 C, d, $^2J_{PC}$ 14, C-3, C-9, C-12), 38.95 (3 C, dd, $^1J_{PC}$ 87, $^2J_{PC}$ 15, C-2, C-10, C-11); δ_P −44.54 (d, J_{PP} 108, P-6), 53.61 (d, J_{PP} 108, P-1); *m/z* (CI) 247 ([M + 1]$^+$, 70%), 190 (100).

1-Hydro-1-phospha-6-phosphoniatricyclo[4.4.4.0]tetradecane trifluoromethanesulfonate 15b. A solution of 1,6-diphosphoniatricyclo[4.4.4.0]tetradecane bis(trifluoromethanesulfonate) (98 mg, 0.19 mmol) in acetonitrile (5 cm^3) was treated with sodium borohydride (21 mg, 0.55 mmol) which caused rapid evolution of hydrogen. The solution was stirred for one hour and evaporated to dryness. The resulting residue was redissolved in water (5 cm^3), then extracted with CH_2Cl_2 (3 × 5 cm^3). The solution was dried ($MgSO_4$) and the solvent removed under reduced pressure to leave a white solid. Recrystallisation from CH_2Cl_2 and Et_2O furnished a white crystalline solid (51 mg, 72%) mp 126–129 °C (Found: C, 40.8; H, 6.7. $C_{13}H_{25}F_3O_3P_2S$ requires C, 41.05; H, 6.6%); $\delta_H(CD_2Cl_2)$ 1.8–2.1 (18 H, m), 2.4–2.5 (6 H, m), 5.64 (1 H, dd, $^1J_{PH}$ 303.0, $^2J_{PH}$ 112, P*H*); δ_C 23.10 (3 C, t, N_{PC} 15, C-5, C-7, C-14), 23.38 (3 C, d, $^2J_{PC}$ 5, C-4, C-8, C-13), 25.74 (3 C, d, $^2J_{PC}$ 6, C-3, C-9, C-12), 28.09 (3 C, dd, $^1J_{PC}$ 90, $^2J_{PC}$ 44, C-2, C-10, C-11); δ_P −83.08 (dd, $^1J_{PP}$ 178, $^2J_{PH}$ 113, P-6), −12.33 (dd, $^1J_{PP}$ 178, $^1J_{PH}$ 303, P-1).

1-Methoxy-1-phospha-6-phosphoniatricyclo[4.4.4.0]tetradecane trifluoromethanesulfonate 14. To a stirred suspension of 1,6-diphosphoniatricyclo[4.4.4.0]tetradecane bis(trifluoromethanesulfonate) (37 mg, 0.07 mmol) in methanol (0.2 cm^3) was added a solution of sodium methoxide in methanol (0.35 mol dm^{-3}, 0.2 cm^3, 0.07 mmol). The solution became homogenous. After two minutes, solvent was removed *in vacuo*, and the residue analysed by NMR. $\delta_H(CD_3CN)$ 2.00 (15 H, br), 2.60 (6 H, br), 3.25 (6 H, br); $\delta_C(CD_3OD)$ 23.0 (3 C, br), 24.5 (3 C, br), 25.0 (3 C, br), 26.5 (1 C, s, *C*H$_3$); δ_P −16.73 (d, $^1J_{PP}$ 158, P-6), 29.90 (d, $^1J_{PP}$ 158, P-1).

1-Fluoro-1-phospha-6-phosphoniatricyclo[4.4.4.0]tetradecane trifluoromethanesulfonate 13. A solution of 1,6-diphosphoniatricyclo[4.4.4.0]tetradecane bis(trifluoromethanesulfonate) (103 mg, 0.195 mmol) in acetonitrile (2 cm^3) was treated with tetrabutylammonium triphenyltin difluoride[41] (175 mg, 0.263 mmol). A white precipitate formed instantly, the solution was stirred for one hour and evaporated to dryness. The resulting residue was dissolved in water (2 cm^3), then extracted with CH_2Cl_2 (3 × 5 cm^3). The solution was dried ($MgSO_4$), and the solvent removed under reduced pressure to leave a white solid. This was recrystallised from CH_2Cl_2 and Et_2O to yield the title compound as a white solid contaminated with tributylammonium trifluoromethanesulfonate; $\delta_H(CD_2Cl_2)$ 1.8–2.8 (24 H, m); δ_F 5.41 (dd, $^1J_{PF}$ 650, $^2J_{PF}$ 150); δ_C 21.52 (3 C, br), 22.32 (9 C, br); δ_P −63.21 (dd, $^1J_{PP}$ 198, $^1J_{PF}$ 718, P-1), −7.82 (t, $^1J_{PP}$ 198, $^2J_{PF}$ 198, P-6). Attempts to separate the title compound from tributlyammonium trifluoromethanesulfonate failed, and therefore an accurate elemental analysis has not been obtained.

1-Phenyl-1-phosphonia-6-phosphabicyclo[4.4.4]tetradecane trifluoromethanesulfonate 17. A suspension of 1,6-diphosphoniatricyclo[4.4.4.0]tetradecane bis(trifluoromethanesulfonate) (255 mg, 0.426 mmol) in THF (10 cm^3) was treated with a solution of phenyllithium in cyclohexane–Et_2O (7:3, 1.8 mol dm^{-3}, 0.75 cm^3, 1.4 mmol). The reaction was sonicated for two hours at 50 °C, and then added to a solution of hydrochloric acid (1 mol dm^{-3}, 5 cm^3). The THF was removed by distillation under reduced pressure, and the remaining aqueous solution was extracted with CH_2Cl_2 (3 × 10 cm^3). The combined extracts were dried ($MgSO_4$), filtered and evaporated to dryness. The resulting white solid was recrystallised from CH_2Cl_2 and Et_2O to give white crystals, which showed a trace (^{31}P NMR)

of 1-phenoxy-1-phospha-6-phosphoniatricyclo[4.4.4.0]tetradecane trifluoromethanesulfonate (120 mg, 63%); $\delta_H(CD_2Cl_2)$ 1.84 (6 H, m, 5-CH_2, 7-CH_2, 14-CH_2), 1.94 (6 H, dm, $^3J_{PH}$ 21, 4-CH_2, 8-CH_2, 13-CH_2), 2.15 (6 H, dm, $^2J_{PH}$ 28, 3-CH_2, 9-CH_2, 12-CH_2), 2.83 (6 H, m, 2-CH_2, 10-CH_2, 11-CH_2), 7.40 (3 H, m, ArH), 7.45 (2 H, m, ArH); δ_C 23.75 (3 C, s, C-4, C-8, C-13), 23.83 (3 C, dd, $^1J_{PC}$ 11, $^2J_{PC}$ 8, C-5, C-7, C-14), 26.79 (3 C, d, $^2J_{PC}$ 9, C-3, C-9, C-12), 33.05 (3 C, dd, $^1J_{PC}$ 82, $^2J_{PC}$ 32, C-2, C-11, C-10), 119.52 (1 C, s, *ipso*-C), 129.36 (2 C, d, J_{PC} 7), 129.77 (2 C, d, $^1J_{PC}$ 8), 130.96 (1 C, s, *para*-C); δ_P −25.47 (d, J_{PP} 46, P-6), −19.05 (d, J_{PP} 46, P-1). Due to the presence of some 1-phenoxy-1-phospha-6-phosphoniatricyclo[4.4.4.0]tetradecane trifluoromethanesulfonate in the recrystallised material an accurate elemental analysis has not been obtained.

1-Benzyl-1-phosphonia-6-phosphabicyclo[4.4.4]tetradecane trifluoromethanesulfonate 16b. A suspension of 1,6-diphosphoniatricyclo[4.4.4.0]tetradecane bis(trifluoromethanesulfonate) (1.53 g, 2.90 mmol) in THF (20 cm^3) was treated with a solution of benzylmagnesium chloride in THF (2.0 mol dm^{-3}, 3 cm^3, 6 mmol). The general procedure and work-up was the same as described for 1-phenyl-1-phosphonia-6-phosphabicyclo-[4.4.4]tetradecane trifluoromethanesulfonate. Recrystallisation from CH_2Cl_2 and Et_2O gave white crystals (420 mg, 31%) mp 182–183 °C (Found: C, 50.8; H, 6.6. $C_{20}H_{31}F_3O_3P_2S$ requires C, 51.1; H, 6.6%); $\delta_H(CD_2Cl_2)$ 1.73 (6 H, m, 5-CH_2, 7-CH_2, 14-CH_2), 1.84 (6 H, dm, $^3J_{PH}$ 21, 4-CH_2, 8-CH_2, 13-CH_2), 1.97 (6 H, dm, $^2J_{PH}$ 28, 3-CH_2, 9-CH_2, 12-CH_2), 2.60 (6 H, m, 2-CH_2, 10-CH_2, 11-CH_2), 3.18 (2 H, dd, $^2J_{PH}$ 10, $^3J_{PH}$ 3, CH_2Ph), 7.2–7.3 (3 H, m, ArH), 7.3–7.4 (2 H, m, ArH); δ_C 23.65 (3 C, t, N_{PC} 18, C-5, C-7, C-14), 23.84 (3 C, s, C-4, C-8, C-13), 26.74 (3 C, d, $^2J_{PC}$ 11, C-2, C-10, C-11), 30.41 (3 C, dd, $^1J_{PC}$ 79, $^2J_{PC}$ 31, C-3, C-9, C-12), 42.84 (1 C, dd, $^1J_{PC}$ 36, $^2J_{PC}$ 29, *C*H_2Ph), 127.38 (1 C, s, *para*-C), 129.37 (2 C, s), 130.22 (2 C, d, J_{PC} 3), 133.45 (1 C, d, $^2J_{PC}$ 6, *ipso*-C); δ_P −27.86 (d, J_{PP} 48, P-6), −12.35 (d, J_{PP} 46, P-1); *m*/*z* (FAB^+) 321 ($M^+ - CF_3SO_3$, 100%), 229 ($M^+ - 1 - CH_2Ph - CF_3SO_3$, 10).

1-Allyl-1-phosphonia-6-phosphabicyclo[4.4.4]tetradecane trifluoromethanesulfonate 18. A suspension of 1,6-diphosphoniatricyclo[4.4.4.0]tetradecane bis(trifluoromethanesulfonate) (1.31 g, 2.48 mmol) in THF (20 cm^3) was treated with a solution of allylmagnesium bromide in Et_2O (1.0 mol dm^{-3}, 5 cm^3, 5 mmol). The general procedure and work-up employed was the same as described above, recrystallisation from CH_2Cl_2 and Et_2O gave white crystals (278 mg, 27%) mp 163–165 °C (Found: C, 45.6; H, 7.0. $C_{16}H_{29}F_3O_3P_2S$ requires C, 45.7; H, 7.0%); $\delta_H(CD_2Cl_2)$ 1.82 (6 H, m, 5-CH_2, 7-CH_2, 14-CH_2), 1.93 (6 H, dm, $^3J_{PH}$ 21, 4-CH_2, 8-CH_2, 13-CH_2), 2.11 (6 H, dm, $^2J_{PH}$ 28, 3-CH_2, 9-CH_2, 12-CH_2), 2.56 (8 H, m, 2-CH_2, 10-CH_2, 11-CH_2, PCH_2CH), 5.3–5.4 (2 H, m, PCH_2CHCH_2), 5.7–5.8 (1 H, m, C*H*); δ_C 23.68 (6 C, br, C-4, C-5, C-7, C-8, C-13, C-14), 26.68 (3 C, d, $^2J_{PC}$ 8, C-3, C-9, C-12), 30.51 (3 C, dd, $^1J_{PC}$ 41, $^2J_{PC}$ 34, C-2, C-10, C-11), 42.09 (1 C, dd, $^1J_{PC}$ 34, $^2J_{PC}$ 31, P*C*H_2CH), 121.82 (1 C, d, $^2J_{PC}$ 6, *C*H), 129.01 (1 C, d, $^3J_{PC}$ 6, PCH_2-CH*C*H_2); δ_P −27.18 (d, J_{PP} 67, P-6), −17.87 (d, J_{PP} 67, P-1); *m*/*z* (FAB^+) 271 ($M^+ - CF_3SO_3$, 32%), 201 ($M^+ - 1 - CH_2$-$CHCH_2 - CF_3SO_3$, 10). A crystal suitable for X-ray analysis was grown by slow diffusion of Et_2O into a solution of the title compound in CH_2Cl_2.

1-Hydro-1-phospha-6-phosponiatricyclo[4.4.3.0]tridecane trifluoromethanesulfonate 15a. To a stirred solution of 1,6-diphosphoniatricyclo[4.4.3.0]tridecane bis(trifluoromethanesulfonate) (136 mg, 0.26 mmol) in acetonitrile (2 cm^3) was added a solution of sodium borohydride (10 mg, 0.26 mmol) in water (0.5 cm^3). A rapid evolution of gas was observed, which subsided after a few minutes. The mixture was stirred for a further two hours, after which time solvent and volatiles were removed *in vacuo* to leave an oily residue. The residue was extracted with CH_2Cl_2 (2 × 2 cm^3) and filtered through a glass sinter. Removal of solvent *in vacuo* left a colourless, oily solid (32 mg, 34%); $\delta_H(CD_2Cl_2)$ 1.05–2.60 (22 H, m), 5.65 (1 H, dd, $^1J_{PH}$ 288, $^2J_{PH}$ 104, P*H*); δ_C 19.09 (1 C, t, $^2J_{PC}$ 8, C-10), 22.27 (1 C, dd, $^1J_{PC}$ 17, $^2J_{PC}$ 5, C-9), 24.86 (2 C, dd, $^1J_{PC}$ 13, $^2J_{PC}$ 8, C-1, C-8), 25.14 (2 C, dd, $^2J_{PC}$ 7, $^3J_{PC}$ 1, C-2, C-7), 25.55 (2 C, d, $^2J_{PC}$ 8, C-3, C-6), 28.32 (1 C, dd, $^1J_{PC}$ 82, $^2J_{PC}$ 64, C-11), 32.76 (2 C, $^1J_{PC}$ 86, $^2J_{PC}$ 45, C-4, C-5); δ_P −32.73 (dd, $^1J_{PP}$ 250, $^2J_{PH}$ 103, P-6), −79.95 (dd, $^1J_{PP}$ 250, $^1J_{PH}$ 282, P-1).

1-Hydrido-1-phospha-6-phosphoniatricyclo[4.4.3.0]tridecane hexafluorophosphate. Potassium borohydride (174 mg, 3.2 mmol) was added to a solution of 1,6-diphosphoniatricyclo-[4.4.3.0]tridecane bis(hexafluorophosphate) (815 mg, 1.6 mmol) in acetonitrile (30 cm^3) resulting in vigorous gas evolution. The reaction mixture was stirred for two hours, and all volatiles were then removed *in vacuo*. The resulting white residue was extracted with dichloromethane (3 × 20 cm^3), and the extracts filtered through a glass sinter before being reduced *in vacuo* yielding a sticky white solid. Recrystallisation from dichloromethane and diethyl ether under anhydrous conditions yielded a colourless, crystalline solid (492 mg, 85%), mp 149–151 °C (Found: C, 36.34; H, 6.33. $C_{11}H_{23}P_3F_6$ requires C, 36.48; H, 6.40%); NMR data as for triflate.

1-Benzyl-1-phospha-6-phosphoniatricyclo[4.4.3.0]tridecane trifluoromethanesulfonate 16a. To a suspension of 1,6-diphosphoniatricyclo[4.4.3.0]tridecane bis(trifluoromethanesulfonate) (250 mg, 0.486 mmol) in THF (5 cm^3) was added a solution of benzylmagnesium chloride in THF (2.0 mol dm^{-3}, 0.5 cm^3, 1 mmol). The general procedure and work-up was as described above. Recrystallisation from CH_2Cl_2 and Et_2O gave an oily solid (103 mg, 46%); $\delta_H(CD_2Cl_2)$ 1.55 (2 H, m, 14-CH_2), 1.7–2.2 (14 H, m, 3-CH_2, 4-CH_2, 5-CH_2, 7-CH_2, 8-CH_2, 9-CH_2, 12-CH_2), 2.40 (2 H, m, 13-CH_2), 2.64 (4 H, m, 2-CH_2, 10-CH_2), 3.03 (2 H, dd, $^2J_{PH}$ 8, $^3J_{PH}$ 2, CH_2Ph), 7.22 (3 H, m, ArH), 7.31 (2 H, m, ArH); δ_C 22.22 (1 C, dd, $^1J_{PC}$ 20, $^2J_{PC}$ 9, C-11), 22.40 (1 C, d, $^2J_{PC}$ 8, C-12), 24.90 (2 C, dd, $^1J_{PC}$ 20, $^2J_{PC}$ 8, C-2, C-10), 25.47 (2 C, s, C-3, C-9), 26.58 (2 C, d, $^2J_{PC}$ 12, C-4, C-8), 27.19 (1 C, dd, $^1J_{PC}$ 73, $^2J_{PC}$ 47, C-13), 33.64 (2 C, dd, $^1J_{PC}$ 81, $^2J_{PC}$ 35, C-5, C-7), 44.01 (1 C, dd, $^1J_{PC}$ 38, $^2J_{PC}$ 28, *C*H_2Ph), 129.12 (1 C, s, *para*-C), 129.12 (2 C, d, J_{PC} 12), 130.46 (2 C, d, J_{PC} 11), 134.35 (1 C, d, $^2J_{PC}$ 6, *ipso*-C); δ_P −42.92 (d, $^1J_{PP}$ 139, P-6), −23.81 (d, $^1J_{PP}$ 139, P-1); *m*/*z* (FAB^+) 307 ($M^+ - CF_3SO_3$, 100%), 215 ($M^+ - 1 - CH_2Ph - CF_3SO_3$, 15). The oily nature of the product prevented an accurate elemental analysis being obtained.

1-Benzyl-1-phospha-6-phosphoniatricyclo[4.4.3.0]tridecane hexafluorophosphate. A solution of benzylmagnesium chloride in tetrahydrofuran (2 mol dm^{-3}, 1 cm^3, 2 mmol) was added to a suspension of 1,6-diphosphoniatricyclo[4.4.3.0]tetradecane bis-(hexafluorophosphate) (300 mg, 0.59 mmol) in tetrahydrofuran (5 cm^3). The mixture was sonicated for one hour, then left to stir overnight. The reaction was quenched by the addition of hydrochloric acid (1 mol dm^{-3}, 3 cm^3, 3 mmol). Volatiles were removed *in vacuo*, leaving an aqueous residue which was extracted with dichloromethane (2 × 10 cm^3). The combined extracts were dried using magnesium sulfate and reduced *in vacuo* yielding an off white solid. Recrystallisation from acetonitrile and diethyl ether furnished a colourless crystalline solid (156 mg, 58%), mp 223–225 °C (Found: C, 47.82; H, 6.49. $C_{18}H_{29}P_3F_6$ requires C, 47.80; H, 6.46%); NMR data as for triflate.

1,*n* + 2-Dialkyl-1,*n* + 2-diphosphoniabicyclo[*n.m.l*]alkane bis(trifluoromethanesulfonates)

1,5-Dimethyl-1,5-diphosphoniabicyclo[3.3.3]undecane bis(trifluoromethanesulfonate) 23a. Solutions of *cis*-1,5-dimethyl-1,5-diphosphacyclooctane (86 mg, 0.49 mmol) and of 1,3-bis-(trifluoromethanesulfonyloxy)propane (166 mg, 0.49 mmol) in CH_2Cl_2 (5 cm^3) were added simultaneously to CH_2Cl_2 (15 cm^3) over two hours with stirring during which time a precipitate began to form. The solution was stirred for a further one hour after which time all volatiles were distilled under reduced pressure to leave a white solid residue which was recrystallised from

acetonitrile and Et_2O to furnish a white solid (199 mg, 83%) mp >300 °C (Found: C, 30.6; H, 5.0. $C_{13}H_{24}F_6O_6P_2S_2$ requires C, 30.2; H, 4.7%); $\delta_H(CD_3CN)$ 1.99 (6 H, d, $^2J_{PH}$ 14, CH_3), 2.32 (6 H, m, 3-CH_2, 7-CH_2, 10-CH_2), 2.55 (12 H, m, 2-CH_2, 4-CH_2, 6-CH_2, 8-CH_2, 9-CH_2, 11-CH_2); δ_C 12.73 (2 C, d, $^1J_{PC}$ 58, *C*H_3), 16.54 (3 C, t, $^2J_{PC}$ 5, C-3, C-7, C-10), 20.48 (6 C, d, $^1J_{PC}$ 44, C-2, C-4, C-6, C-8, C-9, C-11); δ_P 35.93; *m/z* (FAB$^+$) 367 ($M^+ - CF_3SO_3$, 63%), 217 ($M^+ - 1 - 2CF_3SO_3$, 100).

1-Benzyl-5-methyl-1,5-diphosphoniabicyclo[3.3.3]undecane bis(trifluoromethanesulfonate) 23b. Using a similar procedure as described above, solutions of *cis*-1-benzyl-5-methyl-1,5-diphosphacyclooctane (86 mg, 0.29 mmol) and 1,3-bis(trifluoromethanesulfonyloxy)propane (99 mg, 0.29 mmol) in CH_2Cl_2 (5 cm^3) were added simultaneously to CH_2Cl_2 (50 cm^3) over two hours with stirring. The solution was stirred for a further one hour after which time the solid which had formed was filtered off and dried *in vacuo* to furnish a white solid (68 mg, 37%); $\delta_H(CD_3CN)$ 1.68 (3 H, d, $^2J_{PH}$ 14, CH_3), 2.07 (6 H, m, 3-CH_2, 7-CH_2, 10-CH_2), 2.29 (12 H, m, 2-CH_2, 4-CH_2, 6-CH_2, 8-CH_2, 9-CH_2, 11-CH_2), 3.55 (2 H, d, $^2J_{PH}$ 15, CH_2Ph), 7.17 (2 H, m, ArH), 7.29 (3 H, m, ArH); δ_C 12.66 (1 C, d, $^1J_{PC}$ 57, *C*H_3), 16.46 (3 C, t, $^2J_{PC}$ 5, C-3, C-7, C-10), 18.54 (3 C, d, $^1J_{PC}$ 43, C-2, C-8, C-9), 20.38 (3 C, d, $^1J_{PC}$ 43, C-4, C-6, C-11), 33.10 (1 C, d, $^1J_{PC}$ 49, *C*H_2Ph), 128.60 (1 C, d, $^2J_{PC}$ 10, *ipso*-C), 129.76 (1 C, d, $^5J_{PC}$ 3, *para*-C), 130.52 (2 C, d, J_{PC} 3), 131.43 (2 C, d, J_{PC}); δ_P 35.01 (d, $^3J_{PP}$ 5, P-1), 35.60 (d, $^3J_{PP}$ 5, P-5).

1-Benzyl-5-phenyl-1,5-diphosphoniabicyclo[3.3.3]undecane bis(trifluoromethanesulfonate) 23c. Using the same techniques as described earlier, solutions of *cis*-1-benzyl-5-phenyl-1,5-diphosphacyclooctane (400 mg, 1.27 mmol) and 1,3-bis(trifluoromethanesulfonyloxy)propane (431 mg, 1.27 mmol) in CH_2Cl_2 (20 cm^3) were added simultaneously to stirred CH_2Cl_2 (100 cm^3), using a mechanical syringe pump, over two hours. The solution was stirred for a further one hour after which time the solution was filtered and the resulting solid dried *in vacuo* to furnish a white solid. Recrystallisation from acetonitrile and Et_2O gave a white crystalline solid (280 mg, 34%) mp 160–164 °C (Found: C, 43.8; H, 4.8. $C_{24}H_{30}F_6O_6P_2S_2$ requires C, 44.0; H, 4.6%); $\delta_H(CD_3CN)$ 2.09 (6 H, m, 3-CH_2, 7-CH_2, 10-CH_2), 2.40 (6 H, m, 2-CH_2, 8-CH_2, 9-CH_2), 2.64 (6 H, m, 4-CH_2, 6-CH_2, 11-CH_2), 3.60 (2 H, d, $^2J_{PH}$ 16, CH_2Ph), 7.22 (2 H, m, ArH), 7.32 (3 H, m, ArH), 7.64 (2 H, m, ArH), 7.69 (3 H, m, ArH); δ_C 16.68 (3 C, t, $^2J_{PC}$ 5, C-3, C-7, C-10), 18.38 (3 C, d, $^1J_{PC}$ 44, C-2, C-8, C-9), 20.52 (3 C, d, $^1J_{PC}$ 44, C-4, C-6, C-11), 32.92 (1 C, d, $^1J_{PC}$ 49, *C*H_2Ph), 123.46 (1 C, d, $^1J_{PC}$ 12, phenyl-*ipso*-C), 128.56 (1 C, d, $^2J_{PC}$ 9, benzyl-*ipso*-C), 129.74 (1 C, s, benzyl-*para*-C), 130.52 (2 C, s, benzyl), 130.89 (2 C, d, J_{PC} 11, phenyl), 131.41 (2 C, d, J_{PC} 6, benzyl), 131.76 (2 C, d, J_{PC} 9, phenyl), 135.50 (1 C, s, phenyl-*para*-C); δ_P 30.96 (d, $^3J_{PP}$ 5, P-5), 35.35 (d, $^3J_{PP}$ 5, P-1); *m/z* (FAB$^+$) 505 ($M^+ - CF_3SO_3$, 54%), 355 ($M^+ - 1 - 2CF_3SO_3$, 100).

1,5-Dibenzyl-1,5-diphosphoniabicyclo[3.3.3]undecane bis(trifluoromethanesulfonate) 23d. Solutions of *cis*-1,5-dibenzyl-1,5-diphosphacyclooctane (1.25 g, 3.90 mmol) and 1,3-bis(trifluoromethanesulfonyloxy)propane (1.33 g, 3.90 mmol) in CH_2Cl_2 (50 cm^3) were added simultaneously CH_2Cl_2 (50 cm^3) stirred at reflux, using a mechanical syringe pump, over four hours. The solution was stirred at reflux for a further ten hours after which time the solution was filtered and the resulting solid dried *in vacuo* to furnish a white solid. Recrystallisation from acetonitrile and Et_2O gave a white crystalline solid (1.57 mg, 61%) mp 271–273 °C (Found: C, 45.1; H, 4.8. $C_{25}H_{32}F_6O_6P_2S_2$ requires C, 44.9; H, 4.8%); $\delta_H(CD_3CN)$ 2.13 (6 H, m, 3-CH_2, 7-CH_2, 10-CH_2), 2.36 (12 H, m, 2-CH_2, 4-CH_2, 6-CH_2, 8-CH_2, 9-CH_2, 11-CH_2), 3.60 (4 H, d, $^2J_{PH}$ 15, CH_2Ph), 7.24 (4 H, m, ArH), 7.35 (6 H, m, ArH); δ_C 16.37 (3 C, t, $^2J_{PC}$ 6, C-3, C-7, C-10), 18.40 (6 C, d, $^1J_{PC}$ 44, C-2, C-4, C-6, C-8, C-9, C-11), 32.93 (2 C, d, $^1J_{PC}$ 49, *C*H_2Ph), 128.54 (1 C, d, $^2J_{PC}$ 8, *ipso*-C), 129.70 (1 C, s, *para*-C), 130.47 (2 C, s), 131.38 (2 C, d, J_{PC} 3); δ_P 34.21; *m/z* (FAB$^+$) 519 ($M^+ - CF_3SO_3$, 31%), 369 ($M^+ - 1 - 2CF_3SO_3$, 72), 191 (100). A crystal suitable for X-ray analysis was grown by slow diffusion of Et_2O into a solution of the title compound in acetonitrile.

Reaction of *cis*-1,6-dimethyl-1,6-diphosphacyclononane and 1,3-bis(trifluoromethanesulfonyloxy)propane. Solutions of *cis*-1,6-dimethyl-1,6-diphosphacyclononane (123 mg, 0.65 mmol) and 1,3-bis(trifluoromethanesulfonyloxy)propane (220 mg, 0.65 mmol) in CH_2Cl_2 (5 cm^3) were added simultaneously to CH_2Cl_2 (15 cm^3) over two hours with stirring. The solution was stirred for a further one hour after which time the solution was filtered and the resulting solid was dried *in vacuo* to furnish a white solid. Recrystallisation from acetonitrile and Et_2O gave a white crystalline solid which appears to be 1,6,10,15-tetramethyl-1,6,10,15-tetraphosphoniatricyclo[12.4.3.3^{5,9}]tetracosane tetrakis(trifluoromethanesulfonate) or a similar oligomer (99 mg, 29%) mp >300 °C (Found: C, 31.0; H, 5.0. $C_{28}H_{52}F_{12}O_{12}P_4S_4$ requires C, 31.7; H, 5.0%); $\delta_H(CD_3CN)$ 1.8–2.2 (12 H, m), 1.94 (12 H, d, $^2J_{PH}$ 3, CH_3), 2.3–2.5 (12 H, m), 2.5–2.7 (12 H, m), 2.82 (4 H, br); δ_C 5.34 (4 C, d, $^1J_{PC}$ 53, *C*H_2), 12.93 (2 C, s), 15.22 (2 C, s), 17.41 (4 C, d, $^1J_{PC}$ 49), 20.61 (4 C, s), 22.11 (4 C, d, $^1J_{PC}$ 49), 22.94 (4 C, X part of an ABX system, N_{PC} 69); δ_P 35.63.

Reaction of *cis*-1,6-dibenzyl-1,6-diphosphacyclodecane and 1,4-bis(trifluoromethanesulfonyloxy)butane. Solutions of *cis*-1,6-dibenzyl-1,6-diphosphacyclodecane (342 mg, 0.96 mmol) and of 1,4-bis(trifluoromethanesulfonyloxy)butane (340 mg, 0.96 mmol) in CH_2Cl_2 (30 cm^3) were added simultaneously to refluxing CH_2Cl_2 (100 cm^3) over 16 hours with stirring. The solution was stirred for a further two hours after which time the precipitate was removed by filtration and the resulting solid was dried *in vacuo* to furnish a white solid. Recrystallisation from methanol and Et_2O gave a white crystalline solid which appears to be 1,6,11,16-tetrabenzyl-1,6,11,16-tetraphosphoniatricyclo-[14.4.4.4^{6,11}]octacosane tetrakis(trifluoromethanesulfonate) (348 mg, 51%) mp >300 °C (Found: C, 46.4; H, 5.25. $C_{56}H_{76}F_{12}O_{12}P_4S_4$ requires C, 47.3; H, 5.4%); $\delta_H[(CD_3)_2SO]$ 1.46 (8 H, m), 1.82 (16 H, m), 2.04 (8 H, m), 2.49 (16 H, br), 3.83 (8 H, d, $^2J_{PH}$ 15, CH_2Ph), 7.38 (8 H, m, ArH), 7.43 (12 H, m, ArH); δ_C 15.19 (8 C, d, $^1J_{PC}$ 47, C-7, C-10, C-17, C-20, C-21, C-24, C-25, C-28), 18.12 (4 C, d, $^1J_{PC}$ 48, C-2, C-5, C-12, C-15), 19.46 (8 C, d, $^2J_{PC}$ 14, C-8, C-9, C-18, C-19, C-22, C-23, C-26, C-27), 21.66 (4 C, d, $^2J_{PC}$ 17, C-3, C-4, C-13, C-14), 25.97 (4 C, d, $^1J_{PC}$ 46, *C*H_2Ph), 128.28 (4 C, s, *para*-C), 128.45 (4 C, $^2J_{PC}$ 9, *ipso*-C), 129.38 (8 C, s), 129.97 (8 C, J_{PC} 6); δ_P 35.27; *m/z* (FAB$^+$) 1270 ($M^+ - 2 - CF_3SO_3$, 4%), 1122 ($M^+ - 1 - 2CF_3SO_3$, 2), 411 (100).

1,6-Dibenzyl-1,6-diphosphoniabicyclo[4.4.4]tetradecane bromide trifluoromethanesulfonate 21. 1-Benzyl-1-phosphonia-6-phosphabicyclo[4.4.4]tetradecane trifluoromethanesulfonate (180 mg, 0.38 mmol) was heated with benzyl bromide (3.0 g, 1.8 mmol) in a sealed tube for 24 hours at 150 °C. After this time an insoluble brown solid remained which was washed with Et_2O (3 × 20 cm^3) and dried *in vacuo* to leave a brown solid (231 mg, 85%); $\delta_H(CD_3CN)$ 2.09 (12 H, m, 3-CH_2, 4-CH_2, 8-CH_2, 9-CH_2, 12-CH_2, 13-CH_2), 2.50 (12 H, m, 2-CH_2, 5-CH_2, 7-CH_2, 10-CH_2, 11-CH_2, 14-CH_2), 3.62 (4 H, d, $^2J_{PH}$ 15, CH_2Ph), 7.32 (4 H, m, ArH), 7.42 (6 H, m, ArH); δ_C 23.74 (6 C, dd, $^2J_{PC}$ 6, $^3J_{PC}$ 4, C-2, C-5, C-7, C-10, C-11, C-14), 34.09 (2 C, d, $^1J_{PC}$ 47, *C*H_2Ph), 129.54 (1 C, d, $^2J_{PC}$ 8, *ipso*-C), 129.75 (1 C, d, $^5J_{PC}$ 3, *para*-C), 130.61 (2 C, d, J_{PC} 3), 131.61 (2 C, d, J_{PC} 6); δ_P 39.00; *m/z* (FAB$^+$) 561 ($M^+ - Br$, 31%), 411 ($M^+ - 1 - Br - CF_3SO_3$, 37). The hygroscopic nature of the product prevented an accurate elemental analysis being obtained.

1,*n* + 2-Diphosphabicyclo[*n.m.l*]alkanes

1,5-Diphosphabicyclo[3.3.3]undecane 9a. 1,5-Dibenzyl-1,5-diphosphoniabicyclo[3.3.3]undecane bis(trifluoromethanesulfonate) (1.13 g, 1.69 mmol) was treated with a solution of $LiAlH_4$ in THF (1 mol dm^{-3}, 5 cm^3, 5 mmol) and sonicated for 30 minutes and then stirred at room temperature for a further three hours. The reaction was quenched with methanol (2 cm^3)

and evaporated to dryness to leave a solid residue which was extracted with toluene (20 cm^3). The solution was filtered and the solvent removed *in vacuo* to leave a white solid (269 mg, 85%) [Found (EI): $M^+ + 1$, 189.0963. $C_9H_{19}P_2$ requires 189.0962]; $\delta_H(C_6D_6)$ 1.65 (12 H, m, 2-CH_2, 4-CH_2, 6-CH_2, 8-CH_2, 9-CH_2, 11-CH_2), 1.78 (6 H, m, 3-CH_2, 7-CH_2, 10-CH_2); δ_C 19.02 (3 C, t, $^2J_{PC}$ 4, C-3, C-7, C-10), 19.82 (6 C, d, $^1J_{PC}$ 21, C-2, C-4, C-6, C-8, C-9, C-11); δ_P −30.11; *m*/*z* (CI) 189 ($[M + 1]^+$, 15%), 79 (100), 205 ($[M + 1]^+ + O$, 76). 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 three weeks crystals suitable for X-ray crystal structure determination had formed on the upper regions of the tube.

1,5-Diphosphabicyclo[3.3.3]undecane-1,5-dioxide. A solution of 1,5-diphosphabicyclo[3.3.3]undecane in benzene was exposed to the air for 24 hours during which time an insoluble white solid formed. The solid was filtered off and recrystallised from methanol to give 1,5-diphosphabicyclo[3.3.3]undecane-1,5-dioxide [Found (EI): $M^+ + 1$, 221.0855. $C_9H_{19}O_2P_2$ requires 221.0860]; $\delta_H(CD_3CN)$ 1.9–2.0 (18 H, m); δ_C 17.67 (3 C, t, $^2J_{PC}$ 3, C-3, C-7, C-10), 30.41 (6 C, d, $^1J_{PC}$ 60, C-2, C-4, C-6, C-8, C-9, C-11); δ_P 52.90; *m*/*z* (CI) 221 ($[M + 1]^+$, 100%).

1,6-Diphosphabicyclo[4.4.3]tridecane 9c. To a stirred suspension of 1-hydro-1-phospha-6-phosphoniatricyclo[4.4.3.0]tridecane trifluoromethanesulfonate (26 mg, 0.07 mmol) in THF (0.5 cm^3), at −78 °C, was added *n*-butyllithium in hexanes (2 mol dm^{-3}, 0.035 cm^3, 0.07 mmol). The mixture was warmed to room temperature. After five minutes, solvent and volatiles were removed *in vacuo*. The residue was extracted into C_6D_6 and analysed by NMR; $\delta_H(C_6D_6)$ 1.6–2.0 (22 H, m); δ_C 23.93 (1 C, t, $^2J_{PC}$ 3, C-10), 24.00 (2 C, d, $^1J_{PC}$ 30, C-9, C-11), 24.70 (4 C, d, $^1J_{PC}$ 25, C-1, C-4, C-5, C-8), 25.40 (4 C, d, $^2J_{PC}$ 1, C-2, C-3, C-6, C-7); δ_P −21.06; *m*/*z* 216 (M^+, 6%), 190 (100).

1,6-Diphosphabicyclo[4.4.3]tridecane-1,6-disulfide. To the above NMR sample in C_6D_6, was added sulfur (4 mg, 0.17 mmol). The mixture was heated to reflux for one hour. Volatiles were removed *in vacuo*, and the solid residue was analysed by NMR [Found (EI): 280.0646. $C_{11}H_{22}P_2S_2$ requires 280.0638]; $\delta_H(CD_2Cl_2)$ 2.10 (8 H, m), 2.38 (6 H, m), 2.53 (8 H, m); δ_C 20.58 (1 C, s, C-10), 23.15 (4 C, d, $^2J_{PC}$ 6, C-2, C-3, C-6, C-7), 37.02 (2 C, d, $^1J_{PC}$ 41, C-9, C-11), 37.94 (4 C, d, $^1J_{PC}$ 43, C-1, C-4, C-5, C-8); δ_P 50.16; *m*/*z* (EI) 280 (M^+, 23%), 248 (14), 247 (100).

Reaction of 1-hydro-1-phospha-6-phosphoniatricyclo[4.4.4.0]tetradecane trifluoromethanesulfonate 15b with $LiAlH_4$. To a stirred suspension of 1-hydro-1-phospha-6-phosphoniatricyclo[4.4.4.0]tetradecane trifluoromethanesulfonate (84 mg, 0.22 mmol) in THF (2.5 cm^3) at −78 °C, was added a solution of *n*-butyllithium in hexanes (2.2 mol dm^{-3}, 0.1 cm^3, 0.22 mmol). The mixture was warmed to room temperature, and the solution became homogeneous. After five minutes, water was added (4 mg, 0.22 mmol), followed by a little anhydrous Na_2SO_4. The mixture was filtered through a glass sinter and solvents removed *in vacuo* to leave 1,4-*bis*(1-*phospholano*)*butane* as an oily residue (0.027 g, 55%).

Reaction of 1-benzyl-1-phosphonia-6-phosphabicyclo[4.4.4]tetradecane trifluoromethanesulfonate 16b with $LiAlH_4$. 1-Benzyl-1-phosphonia-6-phosphabicyclo[4.4.4]tetradecane trifluoromethanesulfonate (300 mg, 0.63 mmol) was treated with a solution of $LiAlH_4$ in THF (1 mol dm^{-3}, 5 cm^3, 5 mmol). The reaction was stirred with intermittent sonication for 20 hours and worked-up in the same manner as described above to give 1,4-bis(1-phospholano)butane, which has been previously synthesised by a direct route,[9] (52 mg, 35%); $\delta_H(C_6D_6)$ 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-*C*H_2P), 26.76 (4 C, d, $^2J_{PC}$ 4, phospholano-*C*H_2CH$_2$P), 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.

Reaction of 1,6-dibenzyl-1,6-diphosphoniabicyclo[4.4.4]tetradecanediium bromide trifluoromethanesulfonate 21 with $LiAlH_4$. 1,6-Dibenzyl-1,6-diphosphoniabicyclo[4.4.4]tetradecane bromide trifluoromethanesulfonate (231 mg, 0.33 mmol) was treated with a solution of $LiAlH_4$ in THF (1 mol dm^{-3}, 2 cm^3, 2 mmol). After stirring at room temperature, with intermittent sonication, for 24 hours the reaction was quenched with methanol (0.5 cm^3). The product, a clear oil, was isolated as described above (23 mg, 36%), the NMR data was characteristic of 1,4-bis(1-phospholano)butane.

Table 3 Details of structure analysis of **9a**

Crystal data	
Formula	$C_9H_{18}P_2$
M	188.17
Crystal system	Orthorhombic
Space group (no.)	*Pbca* (no. 61)
a (Å)	7.6043(7)
b	12.1881(13)
c	22.158(3)
U (Å^3)	2053.7(4)
Z	8
D_c (g cm^{-3})	1.217
F(000)	816
μ [Mo-Kα (mm^{-1})]	0.364
Wavelength (Å)	0.710 73
Data collection and reduction	
Crystal dimensions (mm)	0.4 × 0.3 × 0.1
2θ range (°)	6.5–50.1
Temperature (K)	173
Total data	8996
Unique data (*NO*)	1812
'Observed' data [$I > 2\sigma(I)$]	1401
R_{int}	0.063
Refinement	
Disordered atoms	None
Least squares variables (*NV*)	100
*R*1 (observed data)	0.045[a]
*wR*2 (observed data)	0.094[a]
S (all data)	1.11[a]
a, *b*[a]	0.0375, 2.36
Final difference map features (e Å^{-3})	+0.34, −0.24

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR = [\Sigma w\Delta^2/\Sigma wF_o^2]^{\frac{1}{2}}$; $S = [\Sigma w\Delta^2/(NO - NV)]^{\frac{1}{2}}$; $\Delta = F_o^2 - F_c^2$; $w = [\sigma^2(F_o^2) + (aP)^2 + bP]^{-1}$, $P = (F_o^2 + 2F_c^2)/3$, $\sigma_c^2(F_o^2)$ = variance in F_o^2 due to counting statistics.

X-Ray experimental

Crystal data and other details of the structure analysis are presented in Table 3.† From a batch of needle-like colourless crystals of **9a**, a single crystal was selected and mounted on a glass fibre with silicone grease. All diffraction measurements were made at −100 °C with a Siemens three-circle SMART[42] area detector diffractometer fitted with a LT-1 cooling device using graphite monochromated Mo-Kα radiation. Unit cell dimensions were determined from reflections taken from 3 sets of 30 frames (at 0.3° steps in ω). A full hemisphere of reciprocal space (1321 frames) was scanned by 0.3° ω steps at $\phi = 0$, 88 and 180° with the area detector centre held at $2\theta = -27°$ each frame exposed for 20 seconds. The reflections were integrated using the SAINT[43] program. A detector and absorption correction was applied on the basis of 2654 symmetry equivalent reflections (maximum and minimum effective transmission coefficients 0.481 and 0.362 respectively). Lorentz and polarisation corrections were also applied. The structure was solved by direct and Fourier methods and refined using full-matrix least-squares refinement on F^2 with the SHELXTL program.[44] All

† 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 207/208.

non-hydrogen atoms were assigned anisotropic displacement parameters and refined without positional constraints. Hydrogen atoms were located in the difference electron density map and assigned idealised positions with isotropic displacement parameters = 1.2 times that of their attached carbon atom. Final difference electron density maps showed no significant features. Complex neutral-atom scattering factors were taken from ref. 45.

Photoelectron spectrum

The He(I) photoelectron spectrum of 1,5-diphosphabicyclo-[3.3.3]undecane was recorded at 57 °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.

Acknowledgements

We thank SERC and Eurothane Ltd. for a CASE award (to C. J. H.), EPSRC for a quota award to D. R. and P. N. T., the DAAD for a NATO grant (to C. G.), Dr M. Murray for assistance with ^{31}P NMR, and Dr K. MacNeil for assistance with mass spectra. R. G. and H. L. are grateful to the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie for financial support, and to A. Flatow for recording the PE spectra. H. L. acknowledges a stipend of the Studienstiftung des Deutschen Volkes.

References

1 J. E. McMurry and T. Lectka, *J. Am. Chem. Soc.*, 1993, **115**, 10 167.
2 For reviews, see: J. G. Verkade, *Acc. Chem. Res.*, 1993, **26**, 483; J. G. Verkade, *Coord. Chem. Rev.*, 1994, **137**, 233.
3 R. W. Alder, *Tetrahedron*, 1990, **46**, 683.
4 R. W. Alder, R. B. Sessions, J. M. Mellor and M. F. Rawlins, *J. Chem. Soc.*, *Chem. Commun.*, 1977, 747.
5 R. W. Alder and R. B. Sessions, *J. Am. Chem. Soc.*, 1979, **101**, 3651; R. W. Alder, A. Casson and R. B. Sessions, *J. Am. Chem. Soc.*, 1979, **101**, 3652.
6 R. W. Alder, C. Ganter, C. J. Harris and A. G. Orpen, *J. Chem. Soc.*, *Chem. Commun.*, 1992, 1172.
7 R. W. Alder, D. D. Ellis, A. G. Orpen and P. N. Taylor, *Chem. Commun.*, 1996, 539.
8 R. W. Alder and D. Read, *Coord. Chem. Rev.*, 1998, in press.
9 R. W. Alder, C. Ganter, M. Gil, R. Gleiter, C. J. Harris, S. E. Harris, H. Lange, A. G. Orpen and P. N. Taylor, *J. Chem. Soc.*, *Perkin Trans. 1*, 1998, 1643.
10 R. W. Alder, R. B. Sessions, A. J. Bennet and R. E. Moss, *J. Chem. Soc.*, *Perkin Trans. 1*, 1982, 603.
11 R. W. Alder, *Tetrahedron*, 1990, **46**, 683.
12 R. W. Alder and S. P. East, *Chem. Rev.*, 1996, **96**, 2097.
13 R. W. Alder, A. G. Orpen and R. B. Sessions, *J. Chem. Soc.*, *Chem. Commun.*, 1983, 999.
14 C. D. Beard, K. Baum and V. Grakauskas, *J. Org. Chem.*, 1973, **38**, 3673.
15 E. Lindner, G. von Au and H.-J. Eberle, *Chem. Ber.*, 1981, **114**, 810.
16 R. W. Alder, C. Ganter, C. J. Harris and A. G. Orpen, *J. Chem. Soc.*, *Chem. Commun.*, 1992, 1170.
17 D. Schomberg, G. Bettermen, L. Ernst and R. Schmutzler, *Angew. Chem.*, *Int. Ed. Engl.*, 1985, **24**, 975.
18 L. E. Carpenter II and J. G. Verkade, *J. Am. Chem. Soc.*, 1985, **107**, 7084; L. E. Carpenter II, B. de Ruiter, D. van Aken, H. M. Buck and J. G. Verkade, *J. Am. Chem. Soc.*, 1986, **108**, 4918.
19 R. W. Alder, N. C. Goode, N. Miller, F. Hibbert, K. P. P. Hunte and H. J. Robbins, *J. Chem. Soc.*, *Chem. Commun.*, 1978, 89; R. W. Alder, *Chem. Rev.*, 1989, **89**, 1215.
20 S. T. D. Gough and S. Trippett, *J. Chem. Soc.*, 1962, 2333.
21 W. J. Bailey and S. A. Buckler, *J. Am. Chem. Soc.*, 1957, **79**, 3567; W. J. Bailey, S. A. Buckler and F. Marktscheffel, *J. Org. Chem.*, 1960, **25**, 1996.
22 L. Horner, F. Röttger and H. Fuchs, *Chem. Ber.*, 1963, **96**, 3141.
23 L. Horner, P. Beck and H. Hoffmann, *Chem. Ber.*, 1959, **92**, 2088.
24 D. P. G. Hamon and G. Y. Krippner, *J. Org. Chem.*, 1992, **57**, 7109.
25 R. C. Hinton and F. G. Mann, *J. Chem. Soc.*, 1959, 2835.
26 P. Brooks, M. J. Gallagher and A. Sarroff, *Phosphorus Sulphur*, *Relat. Elem.*, 1987, **30**, 389.
27 F. Kretch, K. Issleib, A. Zschunke, C. Mügge and S. Skvorcov, *Z. Anorg. Allg. Chem.*, 1991, **594**, 66.
28 B. N. Diel and A. D. Norman, *Phosphorus Sulphur*, *Relat. Elem.*, 1982, **12**, 227.
29 R. W. Alder, M. R. Bryce, N. C. Goode, N. Miller and J. Owen, *J. Chem. Soc.*, *Perkin Trans. 1*, 1981, 2840.
30 K. Schulze, G. Winkler, W. Dietrich and M. Mühlstadt, *J. Prakt. Chem.*, 1977, **319**, 463.
31 R. W. Alder and S. P. East, unpublished results.
32 J. J. Brophy and M. J. Gallagher, *J. Aust. Chem.*, 1969, **22**, 1405.
33 M. J. Doyle, W. Parker, P. A. Gunn, J. Martin and D. D. MacNicol, *Tetrahedron Lett.*, 1970, **3**, 619.
34 The Gaussian 92 program was used: M. J. Frisch, G. W. Trucks, M. Head-Gordon, P. M. W. Gill, M. W. Wong, J. B. Foresman, H. B. Schlegel, K. Raghavachari, M. A. Robb, J. S. Binkley, C. Gonzales, R. L. Martin, D. J. Fox, J. J. P. Stewart, F. W. Bobrowicz, C. W. Rohlfing, L. R. Kahn, D. J. DeFrees, J. Baker and J. A. Pople, Gaussian Inc., Pittsburgh, PA, 1992.
35 E. Heilbronner and A. Schmelzer, *Helv. Chim. Acta*, 1975, **58**, 936.
36 A. Imamura and M. Ohsaku, *Tetrahedron*, 1981, **37**, 2191.
37 A. E. Reed, R. B. Weinstock and F. Weinhold, *J. Chem. Phys.*, 1985, **83**, 735; A. E. Reed and F. Weinhold, *ibid.*, 1983, **78**, 4066.
38 T. Koopmans, *Physica*, 1934, **1**, 104.
39 R. W. Alder, R. B. Sessions, J. M. Mellor and M. F. Rawlins, *J. Chem. Soc.*, *Chem. Commun.*, 1977, 747.
40 R. W. Alder, R. J. Arrowsmith, A. Casson, R. B. Sessions, E. Heilbronner, B. Kovac, H. Huber and M. Taagapera, *J. Am. Chem. Soc.*, 1981, **103**, 6137.
41 M. Gingras, *Tetrahedron Lett.*, 1991, **32**, 7381.
42 SMART Siemens Molecular Analysis Research Tool V4.014 copyright 1989–94, Siemens Analytical X-ray, Madison, WI, USA.
43 SAINT (Siemens Area detector INTegration) program, Siemens Analytical X-ray, Madison, WI, USA.
44 SHELXTL Rev. 5.0, Siemens Analytical X-ray, 1994.
45 *International Tables for Crystallography*, vol. C, 1992, Kluwer, Dordrecht.

Paper 8/00595H
Received 21*st January* 1998
Accepted 5*th March* 1998