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Medium-ring diphosphines: synthesis and transannular chemistry

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Abstract

Medium-ring diphosphines offer unique opportunities to study the interactions between phosphorus atoms. In addition, monocyclic medium-ring diphosphines may be very useful

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ligands in transition metal complexes. A number of useful synthetic routes to these compounds have been developed, but further efforts in this direction might be rewarding.

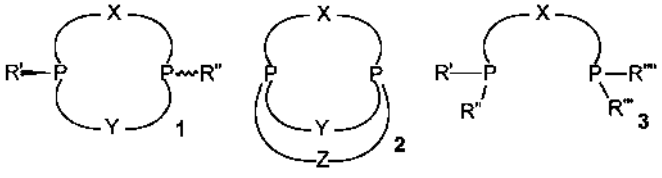
Keywords: Medium-rings; Diphosphines

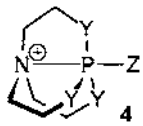
1. Introduction

This review is concerned with compounds in which two phosphorus atoms are incorporated into a medium-sized ring (7–12-membered). Medium-sized rings are usually strained and have a strong tendency to undergo transannular reactions, as discussed later in this introduction. The combination of these features with some of the special properties associated with phosphorus atoms, for example high barriers to inversion [1] and unusual bond lengths and angles compared to first-row elements, suggests that compounds in this category will show novel properties and reactions. The present state of understanding of these compounds is quite primitive and we believe this area is ripe for further development.

Our review will cover the preparation and properties of both monocyclic examples (**1**) and bicyclic compounds which have phosphorus atoms at the bridgeheads (**2**). The former can exist in *cis*- and *trans*-forms, and we will discuss transannular interactions and reactions involving the phosphorus atoms. Bicyclic compounds (**2**) might show *in,out*-isomerism [2], with the separate existence of *in,in*-, *in,out*- and *out,out*-isomers, if phosphorus inversion barriers remain as high as they usually are, and we will discuss interactions and reactions between the bridgehead phosphorus atoms (so-called intrabridgehead chemistry) [3,4]. In addition to their intrinsic interest, *cis*-isomers of compounds with the general formula **1** might be expected to be interesting ligands for transition metal complexes, comparable to, but perhaps usefully different from, the familiar range of chelating diphosphines (**3**), which play such a prominent role as ligands in catalytically-active transition metal complexes.

We will not discuss medium-ring monophosphines, compounds with more than two phosphorus atoms in the ring, or compounds outside the range of 7–12 membered rings except for comparison purposes; phosphazenes will not be discussed at all. We draw attention to several related reviews. Verkade [5,6] has reviewed main group atranes, e.g. **4**, and his work makes an excellent counterpoint





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to our own work on bicyclic diphosphines, and is discussed in Section 4 and Section 5 below. Musker [7] has reviewed the coordination chemistry of medium-ring ligands and, while only one example of a diphosphine is discussed, other systems mainly derived from medium-ring diamines are useful for comparison. Wong [8] has recently reviewed the coordination chemistry of eight-membered polyphosphorus heterocycles.

The special features of medium-ring chemistry are well-established for carbocyclic rings [9]. These compounds are strained, and preferred conformations are typically a compromise between over-large bond angles, poor torsion angles and severe transannular non-bonded interactions. As a result, transannular interactions and reactions are particularly favourable. Many of these features are carried over to heterocyclic analogues and the conformational analysis of medium-ring heterocycles has been extensively discussed [10,11]. Quin [12] has reviewed the conformational properties of medium-ring phosphorus heterocycles, and Gallagher [13] has discussed the conformation and stereochemistry of rings containing phosphorus atoms with particular reference to their ^{31}P-NMR spectra [13,14].

Bicyclic compounds built entirely from medium-rings (7–12-membered) are still quite rare, but all the strain effects already present in monocyclic medium rings are strongly accentuated in bicyclic species [3,4,15]. In particular, the formation of a bond between the bridgehead atoms, leading to a propellane [16–18], is exceptionally favourable. Thus the conversion of the diamine **5** into the dication **6** by oxidation occurs with exceptional ease [19]. This oxidation converts a compound with three 10-membered rings to one with three six-membered rings, all in their preferred chair-form, and undoubtedly relieves a great deal of strain. As a result of this thermodynamic situation, there is potential for the observation of many unusual P . . . P and P . . . X bonding effects with compounds containing phosphorus atoms at one or both bridgehead positions. Thus it has been found possible to observe radical ions like **7** [20–23] and protonated species like **8** [24]; this chemistry is discussed in Section 5 of this review.

2. The synthesis of monocyclic compounds

The general difficulties associated with the closure of medium rings are well-known; these problems result from both enthalpic (strain in the transition state) and entropic effects (decreasing probability of the ends of the chain coming within bonding distance). Nevertheless, most attempts to prepare medium-ring diphos-


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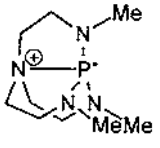
phines have used a ring closure approach, as discussed below. Because of the problems with this approach, alternative ring expansion and ring cleavage strategies are attractive possibilities for the synthesis of medium-ring compounds. Thus the compound bicyclo[3.3.3]octane (manxane), **9**, was prepared [25–27] by two successive ring expansions, while the corresponding amine manxine, **10**, was prepared [27] by the ring cleavage of a propellane precursor which contained only five-membered rings and which could therefore be readily assembled. We discuss ring cleavage approaches to medium-ring diphosphines after ring closure methods; ring expansion routes have not been used to date.

We also note that it might be possible to create the *cis*-isomers of monocyclic medium-ring diphosphines by building them around a templating metal atom. This could be advantageous from the strain point of view, as well as giving entropic advantages; thus a chelated complex of 1,5-diphosphacyclooctane has a bicyclo[3.3.1]nonane framework which should be relatively unstrained. We know of no application of this to diphosphine construction, but an ingenious stereoselective synthesis of 1,5,9-triphosphacyclododecane and tertiary derivatives uses this principle [28].

2.1. Ring closure routes

All the examples of formation of diphosphacycloalkanes by ring closure routes use S_N2 reactions between diphosphines or diphosphide anions and bifunctional alkylating agents, usually dihaloalkanes. An early example is the preparation (Scheme 1) of 1,4-diphenyl-1,4-diphosphacyclohexane by Hinton and Mann [29]. This route utilises two equivalents of both dibenzylphenylphosphine and dibromoethane, and $LiAlH_4$ is used [30,31] to cleave benzyl groups as required. Horner et al. [32] extended the approach in Scheme 1 to the reaction of a series of α,ω-bis(dibenzylphosphino)alkanes with α,ω-dihaloalkanes to form P,P,P,P-tetrabenzyl-1,*n*-diphosphoniacyloalkane dications with ring sizes ranging from seven to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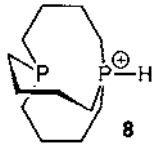
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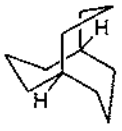

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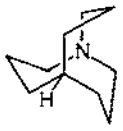

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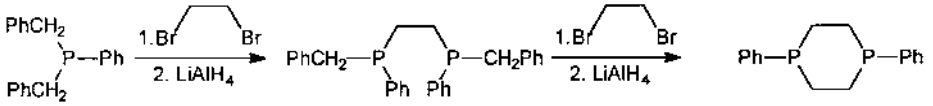
11-membered, e.g. **11**. Yields of these salts ranged from 10 to 60%. Subsequent de-benzylation with $LiAlH_4$ led to the formation of the corresponding neutral diphosphines in 66–90% yields. Little characterisation of these compounds was reported, but in the case of 1,6-dibenzyl-1,6-diphosphacyclodecane **12**, ^{31}P-NMR showed that a 2:1 mixture of stereoisomers was present and an X-ray structure of the dioxide of *trans*-1,6-diphenyl-1,6-diphosphacyclodecane has been reported [33].

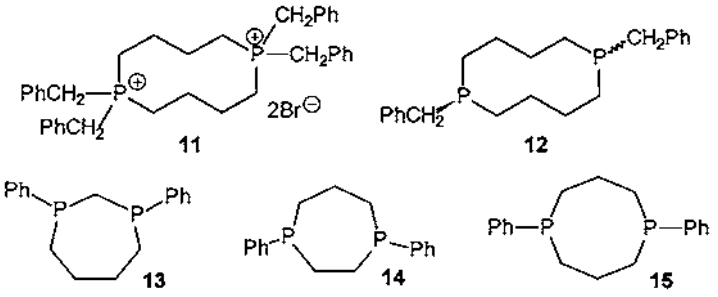
1,3-Diphenyl-1,3-diphosphacycloheptane (**13**) was prepared by Schmidbaur and Schnatterer [34] by reaction of $PhPLiCH_2PPhLi$ with 1,4-dichlorobutane as a mixture of *cis*- and *trans*-isomers. These workers separated the stereoisomers of 1,3-diphenyl-1,3-diphosphacyclohexane by formation of platinum complexes, but unfortunately did not apply this potentially general method to **13**.

Gallagher et al. [35,36] prepared P,P-diphenyl derivatives of 1,3-diphosphacycloheptane, **13**, 1,4-diphosphacycloheptane, **14**, and 1,5-diphosphacyclooctane, **15**. They used the reaction of $PhPLi(CH_2)_3PPhLi$ with the appropriate dichloroalkane to make **13** and **14**. The preparation of **15** was accomplished by reaction of $Ph_2P(CH_2)_3PPh_2$ with 1,3-dibromopropane, followed by hydrolysis of the dication with hydroxide to give 1,5-diphenyl-1,5-diphosphacyclooctane-1,5-dioxide, which was reduced with trichlorosilane to **15**. This route has the advantage of using air-stable intermediates until the final step, but it was found that only one of the stereoisomeric dioxides, probably the *trans*-isomer (see below), was reduced by Cl_3SiH, apparently to a single isomer of the diphosphine. The Gallagher group also reported that direct preparation of **15** from $PhPLi(CH_2)_3PPhLi$ and 1,3-dibromopropane gave a product with a markedly different ^{31}P-NMR spectrum. This was presumed to be the other isomer, but could not be separated from polymeric material.

1,5-Diphenyl-1,5-diphosphacyclooctane (**15**) was also prepared (Scheme 2) by Musker et al. [37] who reacted $Ph_2P(CH_2)_3PPh_2$ with 1,3-diiodopropane under high dilution conditions in DMF to obtain 1,1,5,5,-tetraphenyl-1,5-diphosphoniacyclooctane diiodide in an over 60% yield. After hydrolysis, the isomeric diphos-

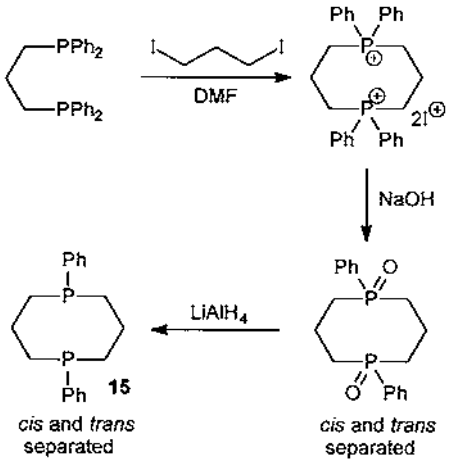


Scheme 1.

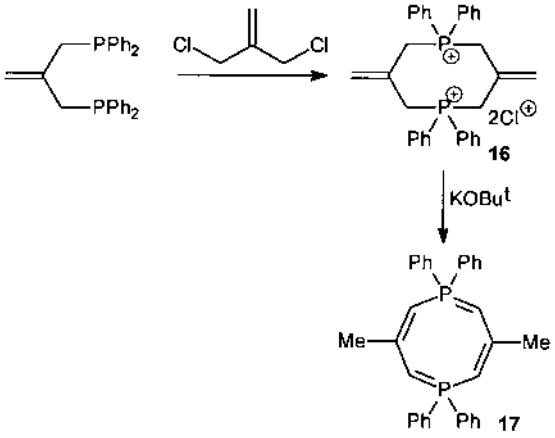


phine dioxides were separated by flash chromatography, and an X-ray structure of the *trans*-isomer was obtained. These workers found that only the *trans*-isomer of the diphosphine dioxides was reduced by Cl_3SiH, but that both isomers of diphosphine **15** were then formed. Reduction was successful with both diphosphine dioxides using $LiAlH_4$ but mixtures of the two isomers of **15** were again obtained. These isomers could not be separated by flash chromatography, fractional sublimation, or crystallisation, but were separated by HPLC and a crystal structure of the *trans*-isomer was obtained.

Schmidbaur and Gamper [38] have described the synthesis of 3,7-dimethyl-1,1,5,5-tetraphenyl-1λ^5,1λ^5-diphosphocin, **17**, which was obtained by treatment of **16** with KO^{t}Bu as shown in Scheme 3. Compound **17**, a 1,5-bis(λ^5-phospha)cyclooctatetraene, was shown by X-ray structure determination to have a tub-shaped eight-membered ring.



Scheme 2.

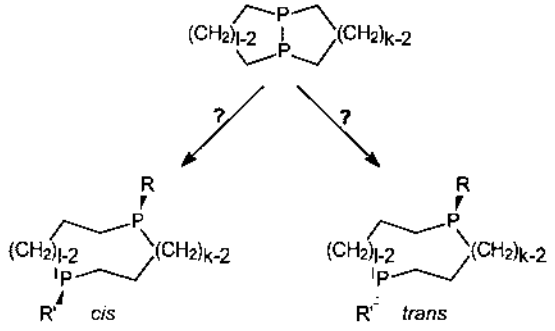


Scheme 3.

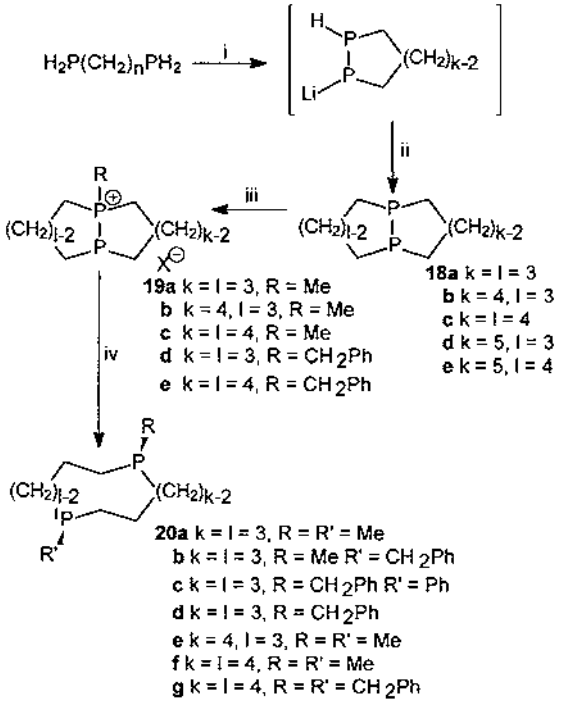
2.2. Ring cleavage routes to medium rings

A useful starting point for a route involving ring cleavage would be a bicyclic system containing a P–P bond. Ideally (Scheme 4), cleavage of the P–P bond could lead to medium-ring diphosphines in either *cis*- or *trans*-forms and with various groups attached to the phosphorus atoms. As discussed below, this ideal scheme is now almost achievable.

Issleib and Thorausch [39] reported the preparation of 1,5-diphosphabicyclo[3.3.0]octane, **18a** (Scheme 5) from 1,3-diphosphinopropane many years ago [39]. The preparation involves a remarkable P–P bond formation in which molecular hydrogen is the by-product. In its original formulation this reaction only gave poor yields, and attempts to cyclise 1,2-diphosphinoethane and 1,4-diphosphinobutane were unsuccessful. However, Alder et al. [40] have shown that optimisation of the reaction conditions, in particular an increase in dilution during



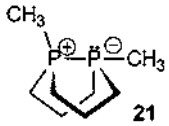
Scheme 4.



Scheme 5.

the initial cyclisation, would allow ring closure of 1,4-diphosphinobutane to 1-lithio-1,2-diphosphacyclohexane, and that in the second (alkylative) ring closure, six- and seven-, as well as five-membered rings could be formed. Thus syntheses of the analogous [4.3.0]-, [5.3.0]-, [4.4.0]- and [5.4.0]-systems were possible.

Alder et al. [41,42] developed a stereoselective route to medium ring *cis*-1,*n*-dialkyl-1,*n*-diphosphacycloalkanes from these bicyclic intermediates. Quaternisation of **18a** with iodomethane occurred in near quantitative yield, and subsequent treatment of **19a** with methyllithium led to the formation of *cis*-diphosphine, **20a**, along with a small amount of the *trans*-isomer. It proved possible to eliminate formation of the *trans*-isomer by substituting methyl triflate for iodomethane in the first step, thus forming the more soluble triflate salt of the intermediate. Reaction with methyllithium then occurred at lower temperatures and led to the exclusive formation of the desired **20a**. Monoquaternary salts can also be prepared using benzyl bromide, and they react stereospecifically with phenyllithium and benzylmagnesium chloride, all reactions being carried out in THF or ether. It seems likely that any alkylating reagent which is reasonably reactive by S_N2 can be used in the first step and thus a range of alkyl and aryl groups can be introduced. These reactions presumably proceed by addition of the alkyl group to the non-quaternised phosphorus atom, followed by P–P bond cleavage in a least-motion manner,



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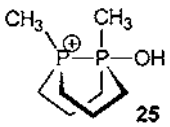

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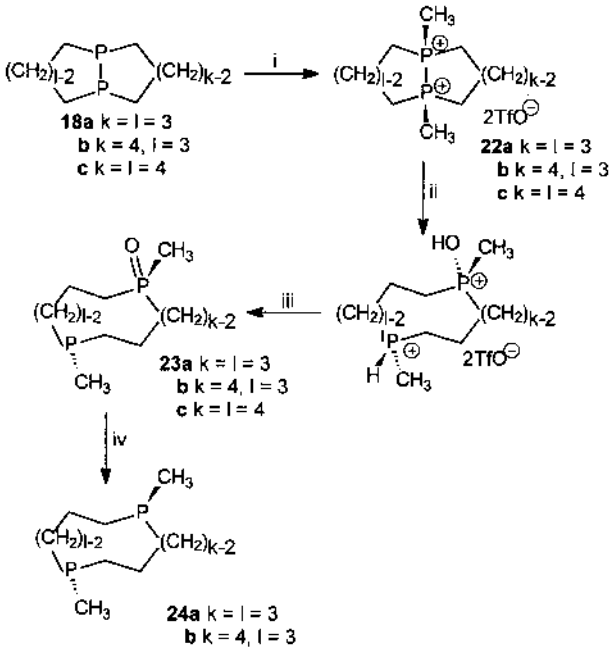
perhaps via an intermediate (**21**). Direct precedents for this P–P cleavage reaction are few, although Kauffmann et al. [43] showed that 1,2-diphenyl-1,2-diphospholane and -1,2-diphosphane do react with alkyllithium reagents with P–P bond cleavage. Other literature examples of P–P bond cleavage result from addition of alkyl halides to tetraalkyldiphosphines [44,45].

Scheme 5 thus provides a potentially very flexible route to medium ring *cis*-1,*n*-dialkyl-1,*n*-diphosphacycloalkanes. While these are probably the most interesting isomers from the point of view of coordination chemistry, a route to the corresponding *trans*-isomers would clearly be desirable. Further alkylation of monoquaternary salts with powerful alkylating agents like methyl triflate gives dications such as **22** (Scheme 6), which are instantaneously hydrolysed by water with the formation, after neutralisation, of monocyclic diphosphine mono-oxides, in which the two exocyclic alkyl groups appear to be exclusively *trans*. A possible intermediate is **25**. Unfortunately, in line with the discussion in Section 2.1 above, all methods of reduction of these dioxides result in some formation of a small proportion (typically 5–10%) of the *cis*- as well as the *trans*-isomer of the monocyclic diphosphine. Thus this ring cleavage route to *trans*-isomers (Scheme 6) would benefit from further optimisation.

3. Structure and properties of monocyclic compounds

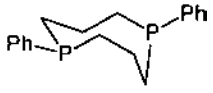
The structures of three medium-ring 1,*n*-dialkyl-1,*n*-diphosphacycloalkanes have been determined by X-ray analysis. *trans*-1,5-Diphenyl-1,5-diphosphacyclooctane has a boat-chair (BC) conformation (**26**) with the phosphorus atoms 4.16 Å apart; the internal C–P–C angles (104.2 and 105.1°) are somewhat larger than typical for phosphines, probably reflecting the effect of the eight-membered ring [37]. The crystal structure of the dioxide of **26** has also been reported [37] as have the structures of the disulfide and diselenide of *trans*-2,6-dimethyl-1,3-dioxo-2,6-diphosphacyclooctane [46]. The structure of *cis*-1,5-dimethyl-1,5-diphosphacyclooctane (**20a**) shows a crown conformation with the P-atoms only 3.86 Å apart. As a consequence of the small P–P distance, the methyl groups in **20a** are virtually-coupled triplets, indicating a large J_{PP} value, and J_{PP} values of 36 and 56 Hz are found for analogues **20b** and **20c** with two different alkyl groups. An interesting feature of the crystal structure of **20a** is that the molecules are stacked with all their lone pairs pointing in one direction (Fig. 1). It may be that the preference for a crown conformation for **20a** is a consequence of crystal packing forces in this



Scheme 6.

stacked structure; MM2 calculations show a very small (0.07 kJ/mol) preference for the normal BC conformation. In the structure of *cis*-1,6-dimethyl-1,6-diphosphacyclodecane (**20f**), the P-atoms are 4.97 Å apart, and J_{pp} is small. The conformation is not the usual BCB structure. Again, this may be the consequence of crystal packing; MM2 calculations show a preference for the BCB conformation, with the observed conformation being the second lowest, 3.4 kJ/mol higher in energy. The structure of the dioxide of *trans*-1,6-diphenyl-1,6-diphosphacyclodecane [33] shows a normal BCB conformation.

The photoelectron spectrum [42] of *cis*-1,5-dimethyl-1,5-diphosphaoctane (**20a**) shows two overlapping bands at 8.5 and 8.8 eV, while that of *cis*-1,6-dimethyl-1,6-diphosphadecane (**20f**) shows one band at 8.0 eV, these bands surely arise from ionisation from the lone pairs at phosphorus. Thus in spite of the close proximity of P-atoms in **20a**, there is very little splitting of the first two bands in the PE



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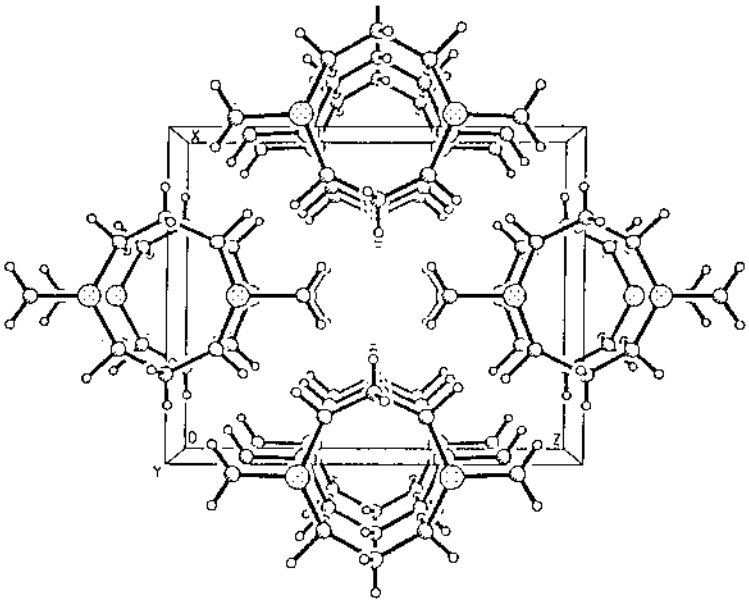
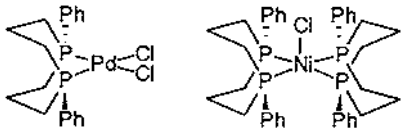


Fig. 1. Packing diagram for *cis*-1,5-dimethyl-1,5-diphosphacyclooctane, showing the molecules in crown conformation stacking with all the lone pairs parallel.

spectrum. This and the coincidence in the case of **20f** is presumed to be due to the high s character of the phosphorus lone pairs and therefore the small spatial overlap between them so there is no evidence of through-bond or through-space coupling.

In light of the intrabridgehead interaction in 1,6-diphosphabicyclo[4.4.4]tetradecane mono oxide (**40**), discussed in Section 5, it is tempting to suggest the difficulties experienced in reduction of *cis*-1,5-diphenyl-1,5-diphosphacyclooctane dioxide might be due to some form of transannular interaction, but there is no direct evidence on this point.

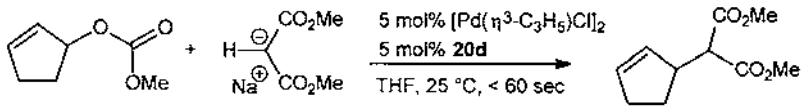
The *cis*-isomers of these medium-ring diphosphines should be chelating ligands, and Arbuckle and Musker [47] have shown this to be the case from X-ray structures of a mono-complex (**27**) of *cis*-1,5-diphenyl-1,5-diphosphacyclooctane with palladium(II) chloride, and a penta-coordinated bis complex (**28**) with nickel(II) chloride. So far little chemistry has been reported with complexes of these ligands, but they might be expected to be comparable to, but perhaps usefully different from, the familiar range of chelating diphosphines (**3**), which play such a prominent role as ligands in catalytically-active complexes. Indeed, in preliminary work (Alder et al., unpublished observations), we have found that *cis*-1,5-dibenzyl-1,5-diphosphacyclooctane (**20d**) functions as a normal chelating diphosphine in a Pd-catalysed reaction between sodium dimethyl malonate and methyl cyclopent-2-en-1-yl carbonate (Scheme 7).



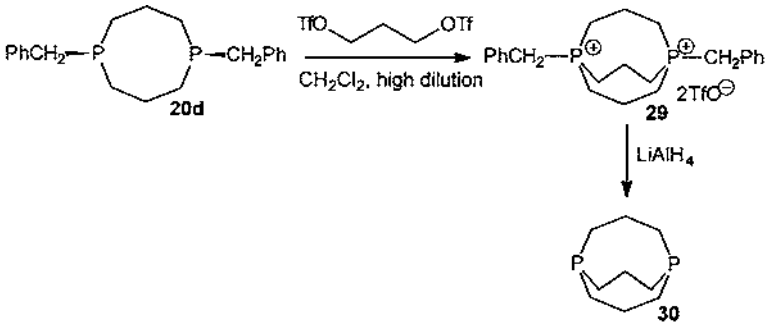
27 28

4. The synthesis of bicyclic compounds

The first bicyclic compounds with phosphorus atoms at both bridgehead positions, 1,4-diphosphabicyclo[2.2.2]octane containing all six-membered rings, was prepared by Hinton and Mann [29] starting from tribenzylphosphine by an extension of Scheme 1 (the reviewers have been told of several attempts to repeat this preparation which have failed). On the other hand, a ring cleavage strategy should be even more advantageous for the synthesis of medium-ring bicyclic compounds with phosphorus atoms at the bridgeheads, in view of the expected increased strain energies in these compounds as compared with monocyclic examples. Nevertheless, 1,5-diphosphabicyclo[3.3.3]undecane, **30** (Scheme 8) has been prepared by a ring-closure strategy. This compound was first reported in 1982 as resulting from radical-induced cyclisation of allylphosphine [48], but this preparation actually yields 1,5-diphosphabicyclo[3.3.0]octane (**18a**) (Norman, personal communication; we have confirmed this re-assignment in Bristol). The successful approach [49,50] (Scheme 8) involves alkylation of 1,5-dibenzyl-1,5-diphosphacyclooctane (**20d**) with the powerful alkylating agent $CH_2(CH_2OTf)_2$ [51,52]. A satisfactory 61% yield of the salt **29** was obtained by using a mechanical syringe pump to carry out the addition under high dilution conditions in CH_2Cl_2, and the benzyl groups were removed in an 85% yield with $LiAlH_4$. The cyclisation step involves the simultaneous closure of two eight-membered rings and the high yield is therefore quite surprising; when the same procedures are applied to the corresponding diamine, 1,5-dibenzyl-1,5-diazacyclooctane, no detectable amount of cyclisation was observed. While it is possible that the ring strain in the product is much less than anticipated, this successful ring closure approach is actually quite limited in scope; increasing the size of just one of the bridges by one methylene group is enough to render this method ineffective. Thus, reaction of 1,6-dimethyl-1,6-diphosphacyclononane (**20e**) with $CH_2(CH_2OTf)_2$ leads to largely polymeric products, and reaction of 1,6-dibenzyl-1,6-diphosphacyclodecane (**20g**) with $(CH_2CH_2OTf)_2$ yielded largely a



Scheme 7.

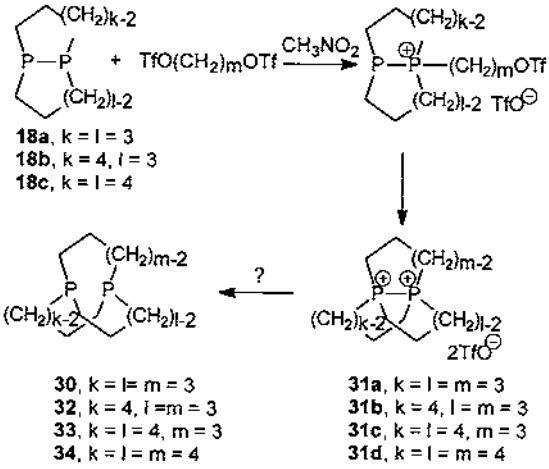


Scheme 8.

dimeric tetraphosphonium product. 1,5-Diphosphabicyclo[3.3.3]undecane (**30**) shows only a single ^{31}P-NMR absorption, and the X-ray structure shows that it exists as the *out,out*-isomer (Section 5).

The obvious ring-cleavage strategy for the preparation of bicyclic diphosphines (Scheme 9) is based on that used successfully to prepare the corresponding diamines by double alkylation of hydrazines. Although this looked straightforward on paper, surprises were in store when it was put into practice. In the first attempt [24], the propellane dication salt 1,6-diphosphoniatricyclo[4.4.4.0]tetradecanedium ditriflate (**31d**) was obtained in rather low yield by alkylation of 1,6-diphosphabicyclo[4.4.0]decane (**18c**) with the powerful alkylating agent $(CH_2CH_2OTf)_2$ in acetonitrile solvent. We were unable to cyclise the product from reaction of **18c** with 1,4-dibromobutane, although this had been successful with the corresponding hydrazine. This is surprising, since it is generally assumed that phosphines are more powerful nucleophiles than the corresponding amines. The next surprise was that it was found that the electron-transfer reduction of this dication did not occur smoothly as it had for the hydrazinium dications (see Section 5.3). An alternative approach via hydride addition to **31d** (Scheme 10) and deprotonation of **35b** led to an unexpected deep-seated rearrangement to **36**.

The preparation of the propellane dication salts was subsequently substantially improved [49,50], in particular by the use of nitromethane in place of acetonitrile as a less nucleophilic solvent, so that a range of these dication salts could be made. An interesting point which emerged was that the largest [4.4.4.0]-system (**31d**) was formed most rapidly and in the highest yield, while the smallest [3.3.3.0]-system (**31a**) was the most difficult to prepare, precisely the reverse of the situation found for the corresponding hydrazines. As a result of these developments, the dications and a range of interesting derivatives (see also Section 5.4) could be prepared, but preparation of the parent diphosphines is still problematical. Alder et al. [50] found that 1,6-diphosphoniatricyclo[4.4.3.0]tridecanedium ditriflate (**31c**) adds hydride like the larger [4.4.4.0]-system, and that treatment of this product with *n*-butyllithium does lead to 1,6-diphosphabicyclo[4.4.3]tridecane (**33**) rather than a rear-



18a, k = l = 3
18b, k = 4, l = 3
18c, k = l = 4

30, k = l = m = 3
32, k = 4, l = m = 3
33, k = l = 4, m = 3
34, k = l = m = 4

31a, k = l = m = 3
31b, k = 4, l = m = 3
31c, k = l = 4, m = 3
31d, k = l = m = 4

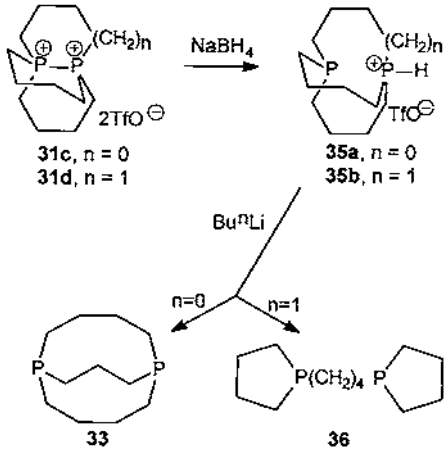
Scheme 9.

rangement product. Although X-ray structural proof of this compound is still awaited, it can be reprotonated to the hydride adduct (see Section 5.5).

Unfortunately, hydride addition to the smaller dication salts **31a** and **31b** is not a clean reaction, and so this approach to the bicyclic diphosphines still has severe limitations.

5. Structure and properties of bicyclic compounds

The only bicyclic medium-ring diphosphine whose structure has been determined



31c, n = 0
31d, n = 1

35a, n = 0
35b, n = 1

33

36

Scheme 10.

is 1,5-diphosphabicyclo[3.3.3]undecane (**30**), a waxy solid which melts at approx. 20°C [50]. This compound adopts an *out,out*-conformation similar to that of manxane [25], with approximate C_{3h} symmetry (Fig. 2). The P . . . P distance is 4.073 Å, which is significantly greater than in the dibenzyl dication salt **29** and the C–P–C angles are smaller than in **29** (106 vs. 110°) although still larger than is normal for phosphines. In the corresponding nitrogen compounds, the reverse is true, 1,5-diazabicyclo[3.3.3]undecane and its 1,8-naphtho-derivative have C–N–C angles close to 120°, which decrease on quaternisation. Undoubtedly, the [3.3.3]-ring system seeks to impose planarity on the bridgehead atoms, but the preference of phosphines for small C–P–C angles is still apparent, and the P–C–C and C–C–C angles are forced to be very large as a consequence (123 and 118°, respectively). Compound **30** reacts with oxygen to give a normal dioxide; reaction with sulphur yields a disulfide which is completely insoluble in all solvents tried. This unusual behaviour is not understood at present, but might indicate a polymeric structure.

As ring sizes increase in these bicyclic diphosphines, it would be expected that *in,out*- and *in,in*-isomers would become relatively more stable, although models suggest that *in,in*-isomers will have very short P . . . P contacts, at least up to 1,7-diphosphabicyclo[5.5.5]heptadecane. The only experimental evidence so far is that 1,6-diphosphabicyclo[4.4.3]tridecane (**33**) shows only a single ^{31}P-NMR absorption, and so cannot be an *in,out*-isomer. We presume it is the *out,out*- rather than *in,in*-isomer and this is supported by the fact that it reacts with sulphur to give a normal disulfide. Molecular mechanics calculations using the MM2 force field predict only a small energy difference between *out,out*- and *in,out* isomers, with the *out,out* more stable by 4.6 kJ/mol; the *in,in*-isomer could not be minimised. On the other hand, PM3 semi-empirical calculations give the following heats of formation: *in,in*: 62.6; *in,out*: 9.08; *out,out*: −94.4 kJ/mol, clearly favouring *out,out*,

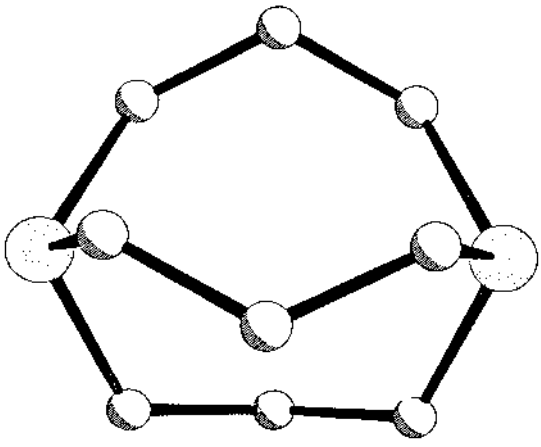


Fig. 2. Structure of 1,5-diphosphabicyclo[3.3.3]undecane.

in agreement with experiment, although it is by no means clear if PM3 should be regarded as more reliable in general for this type of system.

5.1. Photoelectron spectra

The photoelectron spectrum of 1,5-diphosphabicyclo[3.3.3]undecane shows strong splitting (0.56 eV) between the two bands associated with ionisation of P lone pair electrons [50]. Hartree–Fock ab initio calculations with the 6-31G* basis set indicate that this splitting is due almost entirely to through-bond interactions. The much larger splitting (1.5 eV) observed previously for the corresponding diamine [53,54] is partly due to through-space interaction, which contributes approx. 0.7 eV, and partly due to a through-bond effect of 0.8 eV (in earlier publications this latter had been assumed to be unimportant). In the diphosphine (**30**), the phosphorus atoms are too far apart for a significant through-space effect; the overlap between the lone pairs is too small.

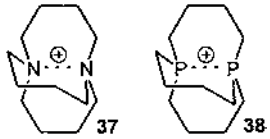
5.2. Dications (propellanes)

The ring-cleavage route described above (Section 4 and Scheme 9) has given access to several propellane dications with P–P bonds (**31a**–**31d**). These compounds are members of a rare class of compounds with two adjacent positively charged atoms. A range of hydrazinium dications are known [3,4,55] but only one other derivative of $H_3PPH_3^{2+}$ is known [56], and this has amino substituents which can accept some of the charge. The structure of **31d** shows it to be a typical [4.4.4]propellane with all the rings in chair form, and a rather normal P–P distance of 2.165 Å [24]. Compound **31d** is quite stable in acidic aqueous solution, like the corresponding hydrazinium dication **6**, but adds nucleophiles (including hydroxide ion) to give products which appear to maintain some degree of P...P bonding (Section 5.4). Despite its apparent similarity to **6**, the electron-transfer behaviour of **31d** is surprisingly different (Section 5.3).

The stability of the tricyclic propellane dications towards hydrolysis by water and hydroxide is strongly dependant on ring size. Propellane dication **31a** (probably the most strained) is similar to dications like **22a** in being instantly hydrolysed by traces of water, whereas **31b**–**31d** are stable in acidic aqueous solutions. Reaction of hydroxide with **31b** is complex, judging from the formation of several peaks in ^{31}P-NMR, but the two larger dications **31c** and **31d** form single products with hydroxide (see Section 5.4).

5.3. Radical ions

One of the outstanding features of the chemistry of bicyclic diamines like **5** was their reversible oxidation to dications like **6**, via radical cations like **37**, which are believed to contain a three-electron σ-bond. Cation **37** forms salts which are air- and water-stable, and the X-ray structure determination of the perchlorate of **37** furnished the first measurement of the length of a three-electron σ-bond [57].

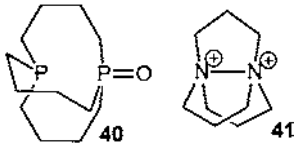


Since $[Me_3P \cdots PMe_3]^{\cdot +}$ and related ions are known in low temperature matrices [58–60], we anticipated that reduction of **31d** would yield a similarly long-lived radical cation. This is very far from being the case. Cyclic voltammetry showed that **31d** was approx. 1 V less easy to reduce than **6**; furthermore, low temperature cyclic voltammetry and pulse radiolysis have convinced us that the lifetime of **38** in fluid solution is very short, probably < 1 μs at room temperature. Radical cation **38** can be observed by γ-radiolysis at low temperature, but the reasons for the remarkable differences between **37** and **38** are far from understood yet. It should be noted that ab initio calculations predict a bond length of 2.8 Å for the $P_2H_6^+$ radical cation [61]. This, taken with the long P–C bonds, probably means that **38** is much more strained than **37**. Calculations also predict the $P_2H_6^+$ radical cation to have lower symmetry that $N_2H_6^+$, but the difference in energy between the lower symmetry structure and a structure with ethane-like symmetry is so small that this seems unlikely to be the source of instability in **38**.

5.4. Addition of nucleophiles to propellane dications

Dication **31d** reacts with a range of nucleophiles (BH_4^-, F^-, MeO^-, PhMgBr, $PhCH_2MgCl$, $H_2C{=}CH{-}CH_2MgBr$) to give adducts **35b**, and **39a**–**39e**, respectively (Scheme 11; **31c** behaves similarly**)**. These adducts all show substantial values for J_{PP}, ranging from 46 (Z = Ph) to 182 Hz (Z = F), leading us to believe that these adducts retained some measure of P . . . P bonding, as indicated by the second resonance form in Scheme 11. Adducts of **31c** show J_{PP} values of 139 and 249 Hz for $Z = CH_2Ph$ and Z = H, respectively. Reaction of **31d** with hydroxide ion leads, via a HO^- adduct, to the neutral mono-oxide of 1,6-diphosphabicyclo[4.4.4]tetradecane (**40**), which shows J_{PP} 108 Hz, suggesting the retention of some P . . . P interaction.

The adducts in Scheme 11 were prepared by addition of nucleophiles to a dication, but are clearly related to the series of adducts **4** prepared by Verkade et

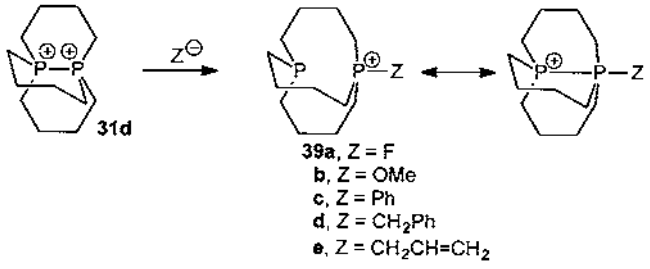


al. [62] by addition of electrophiles to neutral $N(CH_2CH_2Y)_3P$ compounds (Y = O and NR). The Verkade group have determined X-ray structures of a series of these adducts where NR = NMe and have shown that the $P \ldots N_{ax}$ distance varies from 1.967 to 3.33 Å. They have also shown that there is a strong, but not completely linear, correlation between the $P \ldots N_{ax}$ distance and the $N_{eq}–P–N_{eq}$ angle, such that the phosphorus atoms adopt trigonal bi-pyramidal geometry for those adducts with the shorter $P \ldots N_{ax}$ distances [6,62]. The X-ray structures of **35b** (J_{PP} 178 Hz), **39d** (J_{PP} 46 Hz), and **40** (J_{PP} 108 Hz) have been determined so far (Alder et al., unpublished observations); these show P . . . P distances of 2.58, 2.8 and 3.00 Å. It is therefore clear that the J_{PP} value in solution is not a good guide to the P . . . P distance. We intend obtaining X-ray structures for a wider range of adducts, and detailed discussion of these interesting compounds must be deferred. Nevertheless, some similarities and differences between these adducts and those prepared by Verkade, **4**, are already clear. In both series, there is a clear tendency for apicophilic groups to yield short intrabridgehead distances, as might be expected. When **39b** and **40** are treated with acid or with methyl triflate, the dication **31**d is simply regenerated, but Verkade et al. [63,64] have observed dicationic addends where $Z = Et_2O$, $(Et_3Si)_2O$, etc., and the analogous structure to **31a** has not been observed. This might seem surprising since salts of **41** are quite stable, but it may be due to the greater strength of a phosphate P=O, compared with a phosphine P=O bond.

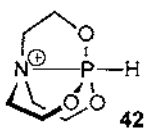
5.5. Proton transfer and phosphorus inversion

Verkade has shown that adducts **4** where Z = H, i.e. **42** [65] and **43a–c** [66] are extremely weakly acidic, requiring strong bases like KO^tBu to liberate the free aminophosphine. They discussed the unexpected finding [67] that **43a** is a stronger base (pK_a 29.6 in DMSO) than either **43b** or **43c**, and that these bases, and **43d**, and particularly **43e** [68], have several potential uses in synthesis [69–71]. They also showed that **44** was a comparably weak acid [72]; this ion bears a strong resemblance to the phosphazene bases studied by Schwesinger [73,74].

For **42**–**44**, protonation is accompanied by some N–P bond formation. It seems reasonable to expect related diphosphines to show P–P bond formation during



Scheme 11.



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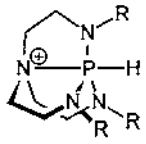
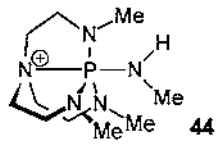


43a, R = H
b, R = Me
c, R = CH_2Ph
d, R = Et
e, R = ^{i}Pr



44

protonation and possible enhanced basicity, but the only known example is 1,8-bis(diphenylphosphino)naphthalene [75], an analogue of Proton Sponge®. Therefore it was not surprising to find that the hydride adducts **35a** and **35b** (Scheme 10) were not deprotonated by bases like 2,7-dimethoxy-1,8-bis(dimethylamino)naphthalene, although pK_a values have not been established yet. As described in Section 4 (Scheme 10), their reaction with the much stronger base ^{n}BuLi is far from straightforward, with **35b** yielding an unexpected rearrangement product. However, **35a** does yield the diphosphine **33** and this process is rapidly reversed at ambient temperature by addition of acid to **33**. Diphosphine (**33**) shows only one ^{31}P-NMR absorption and is almost certainly the *out,out*-isomer, whereas **35a**, like **35b**, shows a very large J_{PP} and must surely have the non-protonated phosphorus inside. It would seem that this protonation results in inversion of the other P atom. Since this occurs at room temperature, the barrier must be very much lower than normal [1]; this clearly merits further investigation.

6. Conclusions

We believe monocyclic medium-ring diphosphines, **1**, may have a promising future as chelating ligands in transition metal complexes. Bicyclic medium-ring compounds with phosphorus atoms at both bridgeheads, **2**, provide a variety of opportunities to study unusual bonding arrangements. It would seem likely that there are still quite a few surprises in store for investigators in this area!

Acknowledgements

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