Bicyclic medium-ring diphosphines: contrasting behaviour in the bicyclo[3.3.3]undecane and bicyclo[4.4.4]tetradecane series

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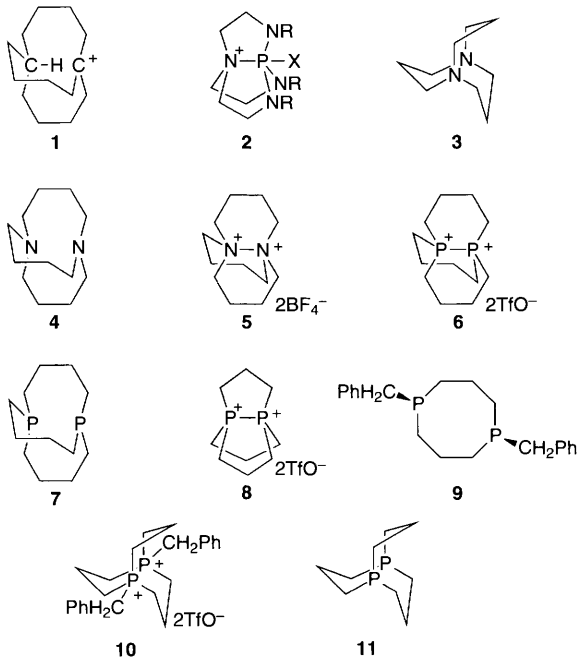
Reaction of *cis*-1,5-dibenzyl-1,5-diphosphacyclooctane 9 with $CH_2(CH_2OTf)_2$ gives 1,5-dibenzyl-1,5-diphosphoniabicyclo[3.3.3]undecanediium bistriflate 10 which is debenzylated with $LiAlH_4$ to 1,5-diphosphabicyclo[3.3.3]undecane 11, but attempts to prepare 1,6-diphosphabicyclo[4.4.4]tetradecane 7 lead to oligomerisation and rearrangement reactions; 1,5-diphosphoniatricyclo[3.3.3.0]undecanediium bistriflate 8 is slowly formed by reaction of 1,5-diphosphabicyclo[3.3.0]octane with $CH_2(CH_2OTf)_2$ in nitromethane, but is hydrolysed much more rapidly than its [4.4.4.0] counterpart.

The interactions between bridgehead atoms in medium-ring bicyclic compounds have provided stable examples of a number of unusual types of bonding. Thus McMurry and Lectka have 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 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]tetradecanediium bistriflate **6** by alkylation of 1,6-diphosphabicyclo[4.4.0]decane with $(CH_2CH_2OTf)_2$ in acetonitrile, but found that this compound could not be reduced to 1,6-diphosphabicyclo[4.4.4.]tetradecane **7**.[6] At that time, we were also unable to extend this preparation of propellane dications to the smaller [3.3.3.0] system. We now report that this problem can be overcome and also that we are able to gain access to 1,5-diphosphabicyclo[3.3.3]undecane by a reaction which simultaneously closes two eight-membered rings with surprising ease. We note other significant differences between the [3.3.3] and [4.4.4] series.



Optimisation of the conditions for the final cyclisation, particularly the use of nitromethane as solvent and purification of the ditriflate reactants by chromatography immediately prior to use, have substantially improved the yield of **6** and allowed us to prepare a series of smaller propellane dications. Thus reaction of 5.2 mmol of 1,6-diphosphabicyclo[4.4.0]decane with 5.7 mmol of $(CH_2CH_2OTf)_2$ in anhydrous nitromethane (10 cm^3) for 24 h gave a 95% yield of **6** (^{31}P NMR, δ −10.6). The rate of formation of the dications decreases sharply in series **6**: ([4.4.4.0] ring system) > [4.4.3.0] (^{31}P NMR, δ +8.8) > [4.3.3.0] (^{31}P NMR, δ +33.9) > 1,5-diphosphoniatricyclo-[3.3.3.0]undecanediium bistriflate **8** (^{31}P NMR, δ +60.7); this is the reverse of the reactivity order for formation of the corresponding hydrazinium dications like **5**.[7] The stability of the products towards water also decreases in the same order; **6** is quite stable below pH 2 and reacts reversibly with hydroxide ion,[6] the [4.4.3.0] and [4.3.3.0] dications can be readily isolated but react irreversibly with hydroxide, while **8** is decomposed rapidly by traces of water in the nitromethane used in its preparation. The reaction of **8** with water gives a complex mixture according to ^{31}P NMR spectroscopy. We suspect that the strain of accommodating the long P–P and C–P bonds produces distorted geometries around the phosphorus atoms in the smaller ring systems, and leads to increased reactivity.

We have developed stereoselective routes to both *cis*- and *trans*-isomers of medium-ring 1,*k*-dialkyl-1,*k*-diphosphacycloalkanes.[8,9] Compounds like *cis*-1,5-dibenzyl-1,5-diphosphacyclooctane **9** are potentially interesting chelating ligands, but we did not anticipate that they would be useful for the generation of medium-ring bicyclic compounds by direct ring closure owing to the strain penalty in generating more medium rings. However, slow simultaneous addition by syringe pump of CH_2Cl_2 solutions (3.8 mmol in 50 cm^3) of **9** and $CH_2(CH_2OTf)_2$,[10] to refluxing CH_2Cl_2 (50 cm^3, medium-dilution conditions) gave a 61% yield of 1,5-dibenzyl-1,5-diphosphoniabicyclo[3.3.3]undecanediium bistriflate **10**. The molecular structure of **10** in the solid as a triflate salt† has approximate C_{3h} symmetry with a P···P distance of 3.690 Å. The conformation of **10** resembles that of manxane[11] (see Fig. 1). Compound **10** (^{31}P NMR, δ 34.2) is debenzylated by a solution of $LiAlH_4$ in thf[12] to produce 1,5-diphosphabicyclo-[3.3.3]undecane **11** in 85% yield.[13] The product shows only one ^{31}P NMR signal at δ −29.4, and must surely be the *out,out*-isomer, since the *in,in*-isomer would be extremely strained. 1,5-Diphosphabicyclo[3.3.3]undecane **11** reacts with an excess of benzyl bromide to return **10**, confirming the structure; the properties and other reactions of **11** are under study.

When *cis*-1,6-dibenzyl-1,6-diphosphacyclodecane **12** is reacted with $(CH_2CH_2OTf)_2$ under similar conditions, the corresponding 1,6-dibenzyl-1,6-diphosphoniabicyclo[4.4.4]un-

decanediium bistriflate **13** is not obtained. The major product (50% yield) gives a ^{13}C NMR spectrum in $(CD_3)_2SO$ which indicates an oligomeric structure: δ 15.2 (double intensity, d, CH_2P, $^1J_{PC}$ 47 Hz), 18.1 (d, CH_2P, $^1J_{PC}$ 48 Hz), 19.5 (double intensity, d, CH_2CH_2P, $^2J_{PC}$ 14 Hz), 21.7 (d, CH_2CH_2P, $^2J_{PC}$ 17 Hz), 26.0 (d, CH_2Ph, $^1J_{PC}$ 46), 128.3, 128.4 (d, $^2J_{PC}$ 9 Hz), 129.4, 130.0. This material is probably the dimeric tetraphosphonium salt **14**; the highest mass peak in the FAB mass spectrum is at *m/z* 1270, which represents [**14** $-CF_3SO_3^-$ $-H_2$]. Macrocyclic tetraphosphines have excited significant interest as ligands,[14] and compound **14** is a potential precursor to a novel caged tetraphosphine; we are investigating its reactions and properties.

It has proved possible to prepare **13** by an alternative route. Reaction of **6** with benzylmagnesium chloride produces 1-benzyl-1-phosphonia-6-phosphabicyclo[4.4.4]tetradecanium triflate **15**. Compound **15** shows a J_{PP} of only 47 Hz, which is small compared to adducts of **6** with other nucleophiles, *e.g.* **16** shows J_{PP} 176 Hz.[6] This suggests a weak P–P interaction owing to the poor apicophilicity of a group like benzyl, but probably does indicate that the non-quaternised phosphorus in **15** is inside-pyramidalised, as expected from the method of preparation and strain energy considerations. Debenzylation of **15** with $LiAlH_4$ gave 1,4-bis(phospholanyl)butane **17**, the same rearrangement product obtained from **16** with Bu^nLi.[6] The mechanism of this surprising rearrangement is unknown, but it probably involves deprotonation from a methylene group α to one phosphorus and subsequent bonding of this carbon to the other phosphorus. We hoped that this rearrangement could be avoided by starting from a compound with the phosphorus atoms *out,out*, as in **13**. Reaction of **15** with benzyl bromide at 150 °C produces **13** in 85% yield, presumably through inversion of the reacting phosphorus centre. Unfortunately, debenzylation of **13** with $LiAlH_4$ also gives the rearrangement product **17** so the first liberated phosphine probably inverts rapidly even at ambient temperature owing to strain relief associated with inward pyramidalisation of the phosphorus. Thus 1,6-diphosphabicyclo[4.4.4]tetradecane **7** still eludes us!

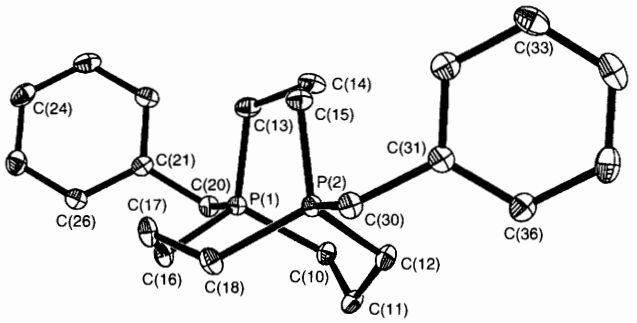
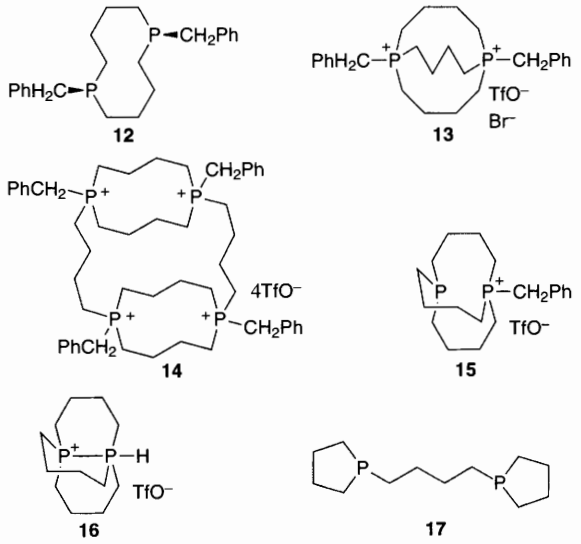


Fig. 1 Molecular structure of **10** with hydrogen atoms omitted for clarity. Important molecular dimensions include: mean bond lengths (Å) (typical individual e.s.d.s 0.002): P–CH_2Ph 1.813, P–CH_2 1.810, C–C 1.525(6); mean bond angles (°) (typical individual e.s.d.s 0.09): PhCH_2–P–CH_2 107.1, CH_2–P–CH_2 111.7.



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Footnote

† *Crystal data* for **10**: $C_{25}H_{32}F_6O_6P_2S_2$, M = 668.6, monoclinic, space group $P2_1/n$ (no. 14), a = 15.901(2), b = 11.170(2), c = 16.588(2) Å, β = 103.74(1)°, V = 2862(1) Å^3, Z = 4, D_c = 1.552 g cm^{-3}, $\bar{\lambda}$ = 0.71073 Å, graphite-monochromated Mo-Kα X-radiation, μ = 0.38 mm^{-1}, $F(000)$ = 1384, T = 173 K. Data were collected on a Siemens SMART CCD area detector diffractometer for a hemisphere of reciprocal space for $3 < 2\theta < 50°$. The structure was solved by direct methods and refined by full-matrix least-squares methods (367 parameters) against all 5039 unique intensity data with $I > 3\sigma(I)$ to final $R1$ = 0.037 for the 4711 reflections with $I > 2\sigma(I)$. Atomic coordinates, bond lengths and angles, and thermal parameters for **10** have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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