

The Preparation and Reactions of 1,6-Diphosphatricyclo[4.4.4.0]tetradecanediium Ditrifluoromethanesulfonate

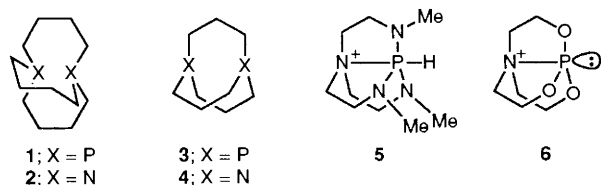
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1,6-Diphosphatricyclo[4.4.4.0]tetradecanediium ditriflate, prepared by the reaction of 1,6-diphospha-bicyclo[4.4.0]decane with 1,4-bis(trifluoromethanesulfonyloxy)butane, is stable in acidic aqueous solutions and reaction with nucleophiles ($X = F^-$, MeO^- , H^-) gives products with $X-P-P^+$ bonding, hydroxide ion giving the diphosphine monoxide but even this retains partial P-P bonding; the hydride adduct reacts with $Bu^{\alpha}Li$ to give 1,4-bis(phospholan-1-yl)butane rather than the expected 1,6-diphospha-bicyclo[4.4.4]tetradecane.

We have shown that experimental studies of σ -bonding and antibonding between two atoms are conveniently carried out when these atoms are the bridgeheads of a medium-ring bicyclic system.¹ We wanted to compare 1,6-diphospha-bicyclo[4.4.4]tetradecane **1**, or related diphosphines like **3**² with

the $N\cdots N$ systems **2** and **4** studied earlier. The diphosphines might show the same unusual redox and protonation behaviour as the diamines (and $[Me_3P\cdots PMe_3]^{++}$ and related ions are known³), but other possibilities could develop due to trigonal bipyramidal P^V bonding. The observation of proto-



nated species like **5**⁴ and radical ions like **6**⁵ hint at some of these possibilities. It is also worth noting that *ab initio* calculations predict the P₂H₆⁺ radical cation to have lower symmetry than N₂H₆⁺.⁶

We aimed to prepare **1** and **3** through their dicationic intermediates **10** and **8** as shown in Scheme 1; this strategy follows that of our successful synthesis of the corresponding hydrazinium dicationic species⁷ and utilises ring cleavage to uncover the medium rings in the final products. However, all attempts to add a third five-membered ring to **7**⁸ have failed so far, perhaps because of the strain in **8** due to the long P–P bond. We also failed to add a final six-membered ring to **9**⁹ using conditions that were successful for preparation of the corresponding hydrazinium dicationic species (AgBF₄ on the bromo-compound). Some changes occur in the NMR spectrum of the intermediate monoalkylated salts when AgBF₄ is added, but these are probably due to coordination of the phosphine to silver. However, reaction of **9** with 1,4-bis(trifluoromethanesulfonyloxy)butane¹⁰ in acetonitrile led to 40% of **10**[†] [$\delta(^{31}\text{P}) - 10.6$], along with products of alkylation of the solvent (the use of less nucleophilic solvents (e.g. CH₂Cl₂ and liquid SO₂) has not so far given greater yields).

The X-ray structure of **10** is shown in Fig. 1.‡ The P–P distance is significantly shorter than in the diphosphine **9**⁹ despite the two adjacent formal positive charges. This might be due to the greater s character in the P–P bond orbitals and/or the compressional strain on this bond of the rings;¹ all the rings adopt the chair conformation as expected, but the long P–P bond causes these chairs to be distorted. One phosphorus atom has a triflate oxygen atom 3.26 Å away and almost on the P–P axis (P–P–O 177.5°), but covalent P–O bonding seems insignificant, since the bond angles at the two phosphorus atoms are almost identical. Dication **10** is completely stable in acidic aqueous solution unlike the less-constrained bicyclic diphosphine dicationic species described in the preceding communication.⁹ Schemes 2 and 3 summarise other reactions and properties of **10**: reaction with fluoride ion was carried out using the reagent Buⁿ₄N⁺Ph₃SnF₂⁻.¹¹ It is noteworthy that the products formed retain a P–P bond in all cases; this is evident from the P–P coupling observed in the ³¹P NMR spectra of the adducts: **11** [$\delta(^{31}\text{P}) - 7.6$, P^{IV}, -64.3, P^V, J_{PP} 182, J_{PF} 697, J_{PPF} 202 Hz]; **12** [$\delta(^{31}\text{P}) - 17.1$, P^{IV}, -27.8, P^V, J_{PP} 155 Hz]; **13**, [$\delta(^{31}\text{P}) - 45.4$, P^{IV}, 55.1, P^V, J_{PP} 115 Hz].

† Satisfactory C and H analyses or HRMS were obtained for all new compounds. ¹H and ¹³C NMR spectra were consistent with the structures assigned.

‡ Crystal data for **10**: C₁₄H₂₄F₆O₆P₂S₃, M = 528.4, monoclinic, space group P2₁/c, a = 8.093(2), b = 23.155(8), c = 12.317(3) Å, β = 104.64(2)°, V = 2233.1(12) Å³, Z = 4, D_c = 1.57 g cm⁻³, μ(Mo-Kα) = 4.59 cm⁻¹, F(000) = 1088, T = 293 K, Nicolet P3m diffractometer, structure solution by direct methods. Full-matrix least-squares refinement for 2343 independent reflections [F > 3σ(F)] collected between 3.0 < 2θ < 48° and 258 parameters converged at R = 0.048, R_w = 0.047 and S = 2.46. All non-hydrogen atoms were refined with anisotropic thermal parameters. H atoms were refined using a riding model with fixed isotropic U. The triflate atoms were refined without positional constraints and anisotropic thermal parameters in the first stage of refinement, but were kept as rigid groups in the final stage of refinement. One triflate group was disordered in the CF₃ part. Atomic coordinates, bond lengths and angles, and thermal parameters, have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

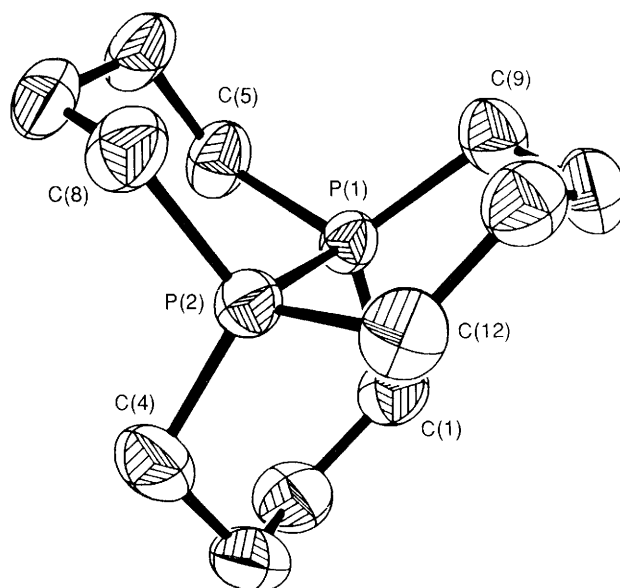
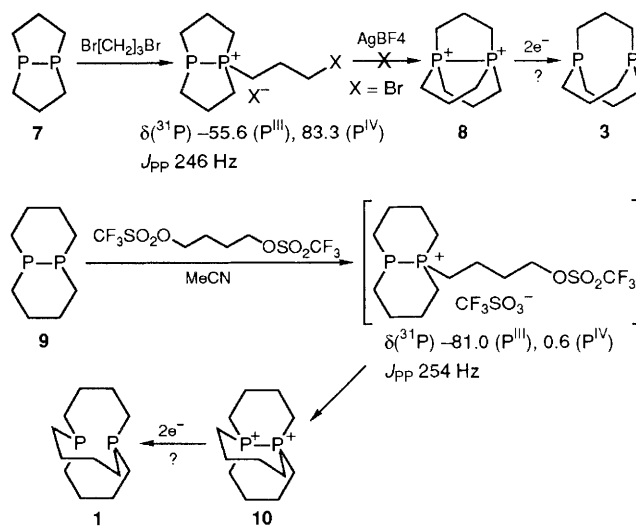
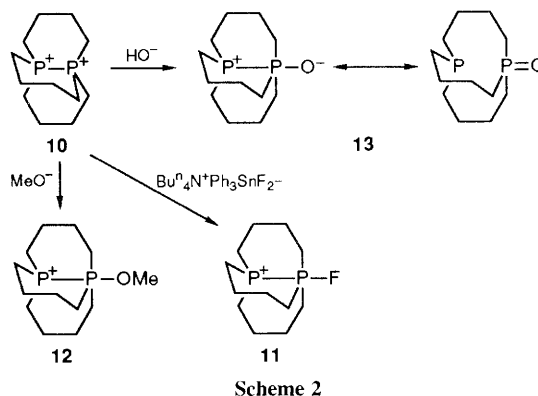


Fig. 1 Molecular structure for dication **10** with hydrogen atoms omitted for clarity; important bond distances (Å) and angles (°) include P(1)–P(2) 2.165(2), P(1)–C 1.802(4) (av.), P(2)–C 1.790(4) (av.), P(2)–P(1)–C 104.0(2) (av.), P(1)–P(2)–C 104.0(2) (av.)



In the case of the H⁻ and F⁻ adducts coupling of the added atom to both phosphorus atoms is observed and the magnitude of the two-bond coupling strongly suggests that the added atom and the P⁺ are apical on the neutral trigonal bipyramidal phosphorus atom. The neutral adduct **13**, which is fully

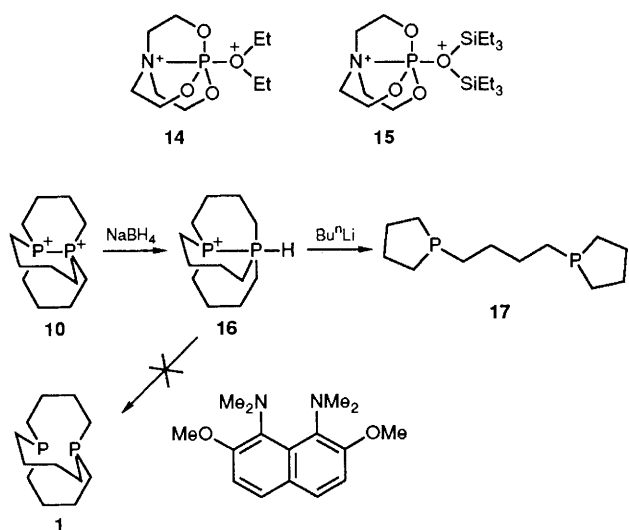


Table 1 Molecular mechanics calculations on 1,6-diphospha-bicyclo[4.4.4]tetradecane

Isomer	MACROMODEL steric energy ^{a/} kJ mol ⁻¹	P...P Distance/Å	C-P-C Angle/°
<i>in, in</i>	242.39	2.858	116.7
<i>in, out</i>	228.38	3.195	110.9 (<i>in</i> -P) 108.8 (<i>out</i> -P)
<i>out, out</i>	261.36	4.873	112.3

^a The implementation of MM2 in MACROMODEL was used: W. C. Still, F. Mohamadi, N. G. J. Richards, W. C. Guida, M. Lipton, R. Liskamp, G. Chang, T. Hendrickson, F. DeGunst and W. Hasel, MacroModel V3.0, Department of Chemistry, Columbia University, New York, NY 10027. Explicit lone pairs were not placed on the phosphorus atoms.

formed at pH 9,¹² appears to have partial P-P bonding and may be regarded as a resonance hybrid of the two forms shown. Formation of the addends **12** and **13** is reversed by addition of triflic acid or methyl triflate. We see no evidence in these reactions for dicationic addends such as compounds **14** and **15** observed by Verkade *et al.*¹³ In fact, the ¹³C NMR spectra of the F⁻ and MeO⁻ adducts are broadened in a way that suggests that addition of these species to the dication may be reversible.

Reduction of **10** with NaBH₄ gives **16**, which is formally the monoprotonated ion of diphosphine **1** (Scheme 3). Compound **16** was recovered unchanged from treatment with one of the strongest known proton sponges 2,7-dimethoxy-1,8-bis(dimethylamino)naphthalene (pK_a ≈ 16.1).¹⁴ This is not too surprising, as Verkade has shown that **5** has pK_a ≈ 16.³ When we treated **16** with BuⁿLi in tetrahydrofuran (THF) a remarkable rearrangement took place and 1,4-bis(phos-

pholan-1-yl)butane **17** [$\delta(^{31}\text{P}) -27.3$] was obtained in 55% (unoptimised) yield. Independent synthesis from 1,4-diphosphinobutane confirmed the structure of this product. While we have no experimental evidence on the mechanism of this rearrangement, deprotonation of a CH₂ group next to one of the phosphorus atoms in **16** is a likely first step.

Why is formation of **1** avoided? Molecular mechanics calculations show all three possible isomers of **1** (*in, in*; *in, out*; and *out, out*) to be extremely strained, owing to the long C-P bonds and the preference for small C-P-C angles. MM2 steric energies indicate that the *in, out*-compound is the least strained of the three isomers (Table 1).

We are now examining the redox and other chemistry of these compounds in detail.

We thank the SERC and Eurothane Ltd for a CASE award (to C. J. H.), the DAAD for a NATO grant (to C. G.), and Dr M. Murray for assistance with ³¹P NMR spectroscopy.

Received, 13th May 1992; Com. 2/02487J

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