Synthesis and Reactions of 1,6-Diphosphabicyclo[4.4.0]decane and Related Molecules

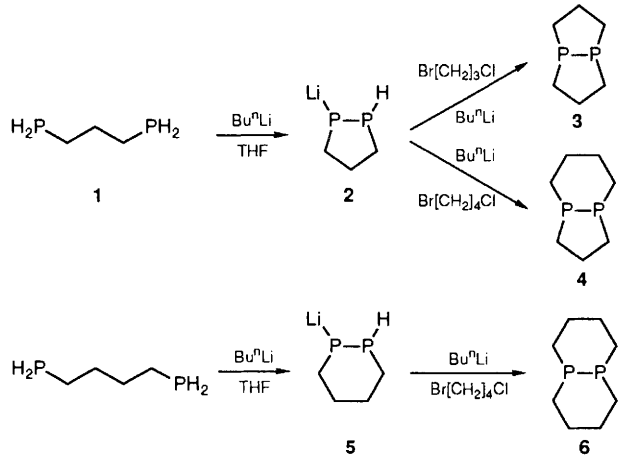
Roger W. Alder,* Christian Ganter, Christopher J. Harris and A. Guy Orpen
School of Chemistry, University of Bristol, Cantock's Close, Bristol BS8 1TS, UK

1,6-Diphosphabicyclo[4.4.0]decane, prepared by way of the cyclisation of 1,4-diphosphinobutane to give 1,2-diphosphacyclohexane, prefers a *cis*-structure to accommodate the long P–P bond; some reactions of this and related bicyclic diphosphines are reported including the conversion into water-sensitive dimethylated dications.

We needed a series of derivatives of H_2PPH_2 with the phosphorus atoms at the bridgeheads of bicyclo[*n.m.*0]-alkanes as intermediates for the synthesis of dicationic propellanes like the 1,6-diphosphatricyclo[4.4.4.0]tetradecanediium ion.[1] Isslieb and Thorausch[2] reported the preparation of 1,5-diphosphabicyclo[3.3.0]octane **3** [$\delta(^{31}P)-27.8$], in ≈15% yield from 1,3-diphosphinopropane **1** (Scheme 1). The route involved one unusual reaction in which treatment of **1** with *n*-butyllithium led to hydrogen evolution and cyclisation to give 1-lithio-1,2-diphosphacyclopentane **2**. Cyclisation of 1,4-

diphosphinobutane by this method led to a complex product mixture; the cyclised product was shown to be present by NMR spectroscopy, but could not be isolated in a pure state. We have found however that cyclisation of 1,4-diphosphinobutane to 1-lithio-1,2-diphosphacyclohexane **5**† does occur in ≈80% yield [by ^{31}P NMR, δ 67.47(*P*H) and 131.15 (*P*Li), J_{PP} 357 Hz, J_{PH} 174 Hz] if concentrations in the cyclisation reaction are reduced by a factor of five (to ≈0.2 mol dm^{-3} in tetrahydrofuran, THF). Further alkylation of **5** by addition of 1-bromo-4-chlorobutane and then another equivalent of *n*-butyllithium yields 1,6-diphosphabicyclo[4.4.0]decane **6** [δ(^{31}P) −77.6], in 40% overall yield (Scheme 1). We have also prepared 1,6-diphosphabicyclo[4.3.0]nonane **4** [δ(^{31}P) −56.9] by similar methods. Isslieb and Thorausch[2] reported quantitative evolution of hydrogen during cyclisation of **1** (we obtained ≈70% of the expected quantity when attempting to reproduce their conditions). However, we see absolutely no hydrogen evolution during the cyclisation to yield **5**, while **1** gives 30% of the theoretical quantity in the same more dilute conditions. We have been unable to determine what other species is being reduced, *e.g.* we can find no *n*-butanol from the possible cleavage of THF.

All three bicyclic diphosphines are formed as *cis*-isomers. This is not surprising for the [3.3.0] and [4.3.0] ring systems, but bicyclo[4.4.0]decanes normally prefer to be *trans*. However, a crystal structure‡ of **6** clearly demonstrates the double-chair *cis*-structure (Fig. 1) with a P–P bond length of 2.19 Å. An interesting feature of the structure of **6** (the molecule lies on a crystallographic twofold axis) is chains of P–P···P–P through the crystal with a P···P intramolecular distance of 3.644 Å. Compound **6** also displays the usual dynamic behaviour of a *cis*-decalin derivative in its ^{13}C NMR spectrum with a coalescence temperature for ring inversion of −27 °C. Conversion of *cis*- into the *trans*-isomer requires inversion at phosphorus and barriers for this are known to be high. In addition in this case inversion at one phosphorus atom would lead to a twist conformation of one ring, resulting in an added energy penalty.[3] Issleib *et al.*[4] prepared the monophosphine 1-phosphabicyclo[4.4.0]decane, and reported that they were unable to effect *cis–trans* interconversion thermally, although they did obtain a 1:1 mixture of the isomers by photolysis. Heating **6** to 300 °C for 4 h led to quantitative recovery of the starting isomer, and even after 4 h at 400 °C most of the material was recovered as the *cis*-isomer, together with some decomposition products; no material that might be the *trans*-isomer could be detected. These conditions are surely extreme enough to overcome the barriers to inversion at phosphorus and to chair–twist interconversion of the six-membered rings. Thus, *cis* is indeed thermodynamically preferred. We believe this is a previously unrecognised effect of long P–P bonds (to a lesser extent the long C–P bonds and small C–P–C angles may also be implicated). Table 1 shows calculated heats of formation from PM3[5] calculations for the



Scheme 1

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

‡ *Crystal data* for **6**: $P_2C_8H_{16}$, M = 174.1, monoclinic, space group $C2/c$, a = 15.513(6), b = 5.535(2), c = 11.554(4) Å, β = 100.37(3)°, V = 975.8(6) Å^3, Z = 4, D_c = 1.185 g cm^{-3}, μ (Mo-Kα) = 3.78 cm^{-1}, F(000) = 376, T = 293 K, Nicolet P3m diffractometer; structure solution by direct methods. Full-matrix least-squares refinement for 894 independent reflections [$F>4\sigma(F)$] collected between $3.0 < 2\theta < 55°$ and 46 parameters converged at R = 0.046, R_w = 0.050 and S = 1.30. All non-hydrogen atoms were refined with anisotropic thermal parameters. H atoms were refined using a riding model with fixed isotropic U. 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.

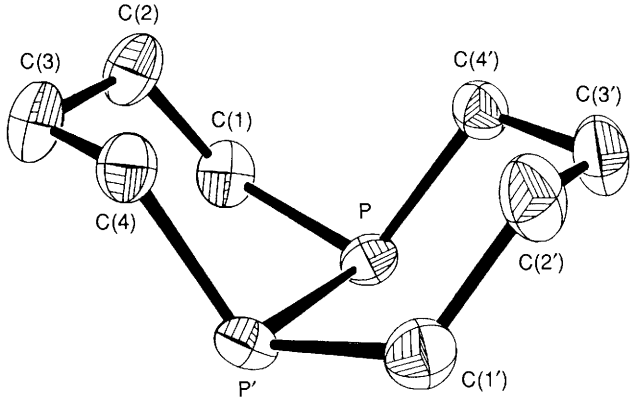
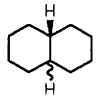
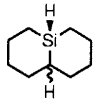
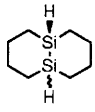
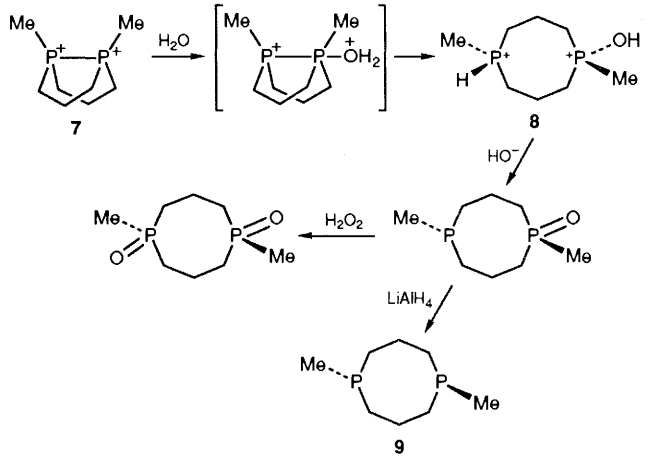


Fig. 1 Molecular structure for **6** with hydrogen atoms omitted for clarity; important bond distances (Å) and angles (°) include P–P' 2.190(1), P–C(1) 1.850(3), P–C(4') 1.841(3), P'–P–C(1) 98.5(1), P'–P–C(4') 102.3(1), C(1)–P–C(4') 103.3(1)

Table 1 Calculated heats of formation

Bicyclo[4.4.0]decane derivative		PM3 ΔH_f/ kJ mol^{-1}	PM3 Bond length[b]/ Å	MM2[a] Steric energy/ kJ mol^{-1}	MM2[a] Bond length[b]/ Å
	*cis*	−178.82		59.12	
	trans	−186.15		47.72	
	*cis*	−144.39	1.90	47.59	1.89
	trans	−139.49	1.89	50.55	1.89
	*cis*	−108.32	2.45	49.59	2.34
	trans	−32.63	2.37	70.91	2.37
	*cis*	−117.65	1.92		
	trans	−109.79	1.91		
	*cis*	−87.82	2.16		
	trans	−36.36	2.16		

[a] The implementation of MM2 in MACROMODEL[6] was used. [b] Length of the internuclear bond.



Scheme 2

two isomers. Lone pair–lone pair interactions are apparently not responsible because the same preference for *cis*-geometry is predicted for 1,6-disilabicyclo[4.4.0]decane by both PM3 and MM2 (MACROMODEL MM2[6] is not parameterised for P–P bonds). It should also be noted that the corresponding hydrazine (1,6-diazabicyclo[4.4.0]decane) is known to adopt the *trans*-geometry in the gas phase,[7] in solution[8] and as a crystalline hydrate.[9] We observed a related preference for *cis*-geometry in monoprotonated 1,6-dimethyl-1,6-diazacyclodecane, in which the intrabridgehead bond in the decalin structure is an N···H–N$^+$ bond 2.60 Å long.[10]

Compounds **3**, **4** and **6** are readily converted into disulfides; X-ray studies confirm the *cis*-geometry in each case.[11,12] Isslieb and Thorausch[2] reported the monomethylation of **3**, and monomethylated salts can also be obtained from reaction of **4** and **6** with iodomethane. Reaction of these diphosphines with an excess of methyl trifluoromethanesulfonate (triflate) yields dimethylated dications, the first examples of hexaalkylated dicationic derivatives of H_2PPH_2.[13] These compounds are stable to oxygen but are very sensitive to water, being instantly hydrolysed even by the traces of water in commercial CD_3CN. Hydrolysis of 1,5-dimethyl-1,5-diphosphabicyclo[3.3.0]octanediium ditriflate **7** [$\delta(^{31}P)$ 54.0], proceeds as shown in Scheme 2, the initial product isolated being a diprotonated salt of a diphosphine monoxide **8** [$\delta(^{31}P)$ 5.4 (J_{PH} 505 Hz), and 83.8]; the other dication salts behave similarly. After neutralisation, the diphosphine monoxides can be oxidised to dioxides and reduced to diphosphines. The 1,5-dimethyl-1,5-diphosphacyclooctane **9** [$\delta(^{31}P)$ −39.4], formed by $LiAlH_4$ reduction of the eight-membered ring diphosphine monoxide is the *trans*-isomer since examination of the ^1H NMR signal for the β-CH_2 groups in the ring shows these protons to be equivalent. This stereochemistry is in accord with the mechanism shown in Scheme 2, which involves inversion at one phosphorus and retention at the other; it also agrees with our observations of the partial (and much slower) hydrolysis of the 1,6-diphosphatricyclo[4.4.4.0]tetradecanediium dication reported in the following paper.[1] In the present cases, the initial coordination of a water molecule and subsequent deprotonation can be followed by cleavage of the P–P bond and protonation of the phosphine liberated. In the propellane series, cleavage of the intrabridgehead P–P bond not only leads to a considerable increase in strain, but is effectively unproductive unless the released phosphine could be inside-protonated or invert to accept a proton from the outside, both of which are very unlikely.

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