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Synthesis and Structures of Isomeric Diphenylphosphinoamino-Substituted Cyclodiphosph(III)azanes

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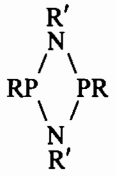
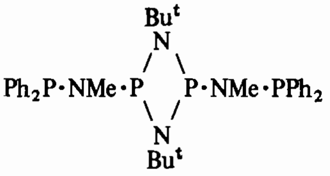
The chemistry of the cyclodiphosph(III)azanes (1) (R = alkylamino, alkoxy; R′ = alkyl, aryl, Me_3Si) has recently formed the subject of several investigations, with the effects of geometrical isomerism [1–3], and the relationship with the phosph(III)-azenes [2,4,5], RP = NR′, receiving special attention.



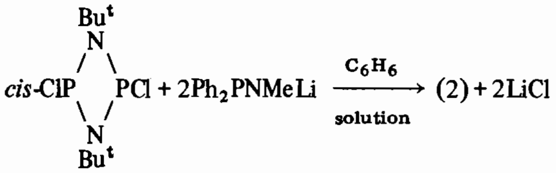
(1)

So far, only relatively simple amino- [1, 3, 6] or silylamino-derivatives [2, 5] have been obtained, but we have now synthesized a diphenylphosphino-derivative (2), which is a tetraphosphine, and examined its solution and solid-state structure.



(2)

Compound (2) was synthesized as a *ca.* 2:1 mixture of isomers (70% yield) by the route:



The N-lithiated aminophosphine was obtained by addition of n-butyl lithium (as a solution in hexane) to $Ph_2P·NHMe$ in benzene solution. The two isomers, m.p. 170–3° and 190–2 °C, were purified by fractional crystallisation from light petroleum (b.p. 40–60 °C)/methylene chloride mixtures (the major isomer having the lower melting point and being much more soluble) and their stoichiometry was established by elemental analyses. The $^{31}P-\{^1H\}$ n.m.r. spectra of the two isomers indicate that they are based on structure (2), rather than that of a phosph(III)azene, $Ph_2PMNeP{=}NBu^t$. For example, the spectrum of the isomer m.p. 170–3 °C is typical of an AA′XX′ spin system and is readily simulated (Fig. 1). This also is true of the second isomer. There are no low-field signals ($\delta_P \gtrsim +300$) that would be expected for a phosph(III)azene. The endo ^{31}P signals of the isomers m.p. 170–3° and 190–2 °C have shifts typical of mutual *cis*-, and *trans*-arrangements of the phosphorus substituents respectively [1]. $^1H-\{^{31}P\}$ double resonance experiments also show that the *exo-PNP* coupling constant is positive in both cases. This, together with the small, *PNCH*, spin couplings (assumed positive) indicates that the preferred conformations about the *exo* P–N bonds are those shown in (3) [7, 8].

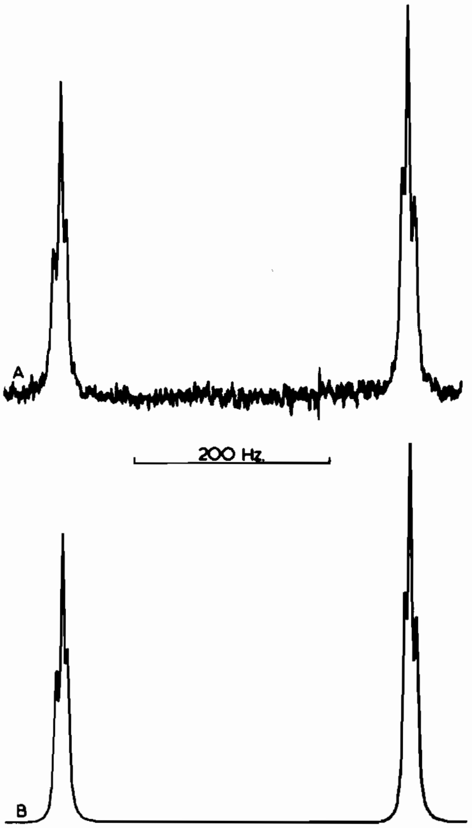
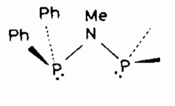


Fig. 1. Low-field half of the 40.5 MHz pulsed Fourier Transform $^{31}P-\{^1H\}$ n.m.r. spectrum of *cis*-(2). Frequency increases from right to left. A, Observed; B, Simulated, using the parameters in the Table, and the SIMEQ II program of C. W. F. Kort and M. J. A. de Bie.

TABLE. ^{1}H and ^{31}P N.m.r. data for Isomers of (2).

Isomer	δ(H)^a	^{3}J(*P*NC*H*) (Hz)	δ(P)^b	^{2}J(PNP) (Hz)	^{4}J(PNPNP) (Hz)
cis m.p. 170–3 °C	2.78 (NCH_3) 1.23 (CCH_3)	+2.6 (*endo* P)^c +2.6 (*exo* P)	+116.7 (*endo* P) +49.8 (*exo* P)	12.2 (*endo*)^e +356	–0.5
trans m.p. 190–2 °C	2.83 (NCH_3) 1.00 (CCH_3)^d	+2.3 (*endo* P)^c +2.3 (*exo* P)	+205.7 (*endo* P) +47.7 (*exo* P)	13.8 (*endo*)^e +357	–0.5

^{a}CDCl$_3$ solutions at *ca.* 30 °C. ^{b}C$_6$D$_6$ solutions at *ca.* 30 °C; shifts are downfield from external 85% H$_3$PO$_4$. ^{c}^{3}J(*P*NC*H*) + ^{5}J(*P*NPNC*H*); these couplings are assumed positive, see ref. 8. ^{d}|^{4}J(*P*NCC*H*)| = 0.8 Hz. ^{e}Sign not determined.



Single crystal X-ray analysis of (2) m.p. 170–3 °C, based on 765 diffractometric intensities refined to R = 0.077, indicates that the cyclodiphosph(III)-azane ring is retained in the solid state (Fig. 2).* The ring is normal to a crystallographic mirror plane which passes through the endo nitrogen atoms N(1) and N(2). The puckering of the ring, revealed by displacements of ± 0.13 Å of alternate atoms from the mean P(1)N(1)N(2)P(1′) plane, is very similar to that found in (C$_5$H$_{10}$NPNBu^t)$_2$ [1]. The exo nitrogen atoms, N(3) and N(3′), lie *cis* with respect to the ring so that there is a close intramolecular approach between the N-methyl groups [C(7)...C(7′) 3.43 Å]. The distribution of bonds at N(3) is close to trigonal-planar (sum of bond angles = 359°); the co-ordination plane, defined by the atoms N(3), P(1), P(2), and C(7), bisects the angles C(8)–P(2)–C(14) and N(1)–P(1)–N(2). The relevant torsion angles are C(7)–N(3)–P(2)–C(8) and –C(14) 52(1) and –55(1)° and C(7)–N(3)–P(1)–N(1) and –N(2) –44(1) and 42(1)° respectively. There is thus good agreement with the conformation (3) predicted by n.m.r. As in other aminocyclodiphosph(III) azanes [1, 5], the *exo* P(1)–N(3) [and P(1′)–N(3′)] bonds are shorter than the *endo* P–N bonds; the reverse is true of the aminocyclophosphazenes [9] where the *endo* P–N bonds have considerable multiple character.

Generally, there is a marked tendency for *cis*-isomers of (1) (R = alkylamino, R′ = Bu^t) to be thermodynamically favoured [1], with a rapid *trans* → *cis* isomerisation occurring, particularly in polar solvents. No isomerisation of (2) has been observed in chloroform solution at ambient temperatures, but at *ca.* 60 °C almost complete *trans* → *cis* isomerisation occurred over a period of three days. This was accompanied by the formation of several unidentified decomposition products. The isomers of (2), which have known preferred conformations in solution, are particularly interesting as potentially tetradentate ligands.

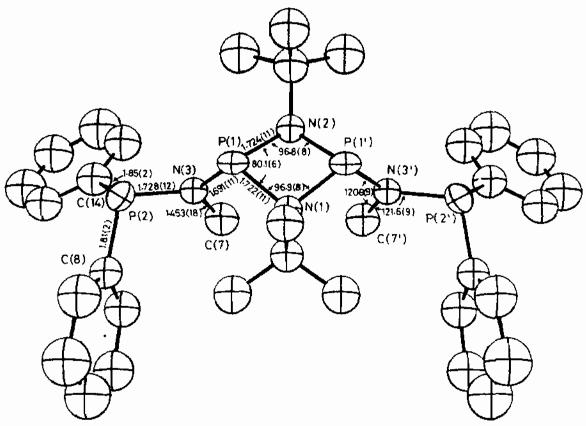


Fig. 2. The molecular structure of *cis*-(2) showing selected bond lengths (Å) and angles (°). The P(1)–N(3)–P(2) angle is 116.2(6)°. The labels of the phenyl and t-butyl carbon atoms are omitted for clarity. Primed atoms are related to the corresponding unprimed atoms by a crystallographic mirror plane passing through N(1) and N(2) and normal to the P$_2$N$_2$ ring.

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*The crystals are orthorhombic, space group *Pbnm* (D_{2h}^{16} – No. 62) with 4 molecules in a cell of dimensions a = 10.197, b = 12.495, c = 27.988 Å.