Synthesis and Conformational Studies of (Diphenylphosphinoamino)cyclodiphosph(m)azanes

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A series of 2,4-bis(diphenylphosphinoalkylamino)-1,3-di-t-butylcyclodiphosph(III)azanes, $[(Ph_2P)RNPNBu^t]_2$ [R = Me or Et (*cis*- and *trans*-isomers); R = Prⁱ or Bu^t (*cis*-isomers)], have been prepared by the reactions of *N*-lithiated alkyl-*N*-(diphenylphosphino)amines, N(PPh₂)(R)(Li), with 2-*cis*-4-dichloro-1,3-di-t-butylcyclodiphosph(III)azane, (CIPNBu^t)₂, in benzene solution. Hydrogen-1, ¹³C, and ³¹P n.m.r. spectroscopy show that these compounds are cyclodiphosph(III)azanes rather than phosph(III)azenes, (Ph₂P)RNP=NBu^t, in solution, and variable temperature ³¹P n.m.r. data have enabled the preferred conformations of the *exo*-P⁻N-P skeletons to be identified. In the case of [(Ph₂P)RNPNBu^t]₂ (R = Prⁱ and Bu^t) more than one conformer can be distinguished at sub-ambient temperatures.

THE relationships between monomeric phosph(III)azenes, RP=NX ($R = amino, X = alkyl, SiMe_3, etc.$), and the analogous cyclodiphosph(III)azanes, (RPNX)2, have been studied recently.1-3 Phosph(III)azenes are stabilised by the presence of relatively bulky R and X substituents, for example in $(Me_3Si)R'NP=NR'$ $(R'=Bu^t or$ SiMe₃),^{1,2} R''P=NBu^t ($\mathbf{R}'' = 2,2,6,6$ -tetramethylpiperidinyl),⁴ and to a lesser extent, when the phosph(III)azene forms part of a five-membered ring.^{5,6} In the cyclodiphosph(III)azanes, $(RPNX)_2$ [R = Bu^t, Ph, or SiMe₃; $X = NR'_2$, OR' (R' = alkyl) etc.], geometrical isomers have been identified and these have marked differences in chemical and physical properties.⁷⁻¹⁰ The reasons for these differences have not been clearly established, although ring-puckering effects in the cis isomers may be important.¹¹ We now report on the synthesis of a series of diphenylphosphinoaminosubstituted cyclodiphosp(III)azanes, (1) (R = alkyl), in which the possibility of phosph(III)azene formation is



considered. Configurational isomerism arising because of different orientations of the substituents on the ring (endo) phosphorus atoms produces cis- and trans-isomers (1). Also, conformational isomerism arises from differing orientations within the exocyclic (exo) PNP skeletons. The latter effect has been probed using recently established empirical correlations between the magnitude of PNP,¹² PNC, and PNCH ¹³ spin couplings and conform-

ations around P^{III–N} bonds. A preliminary report of the synthesis of (1) (R = Me) has appeared.¹⁴

RESULTS AND DISCUSSION

The synthesis of compound (1) (R = Me) was investigated by routes (*i*)—(*iii*), the lithiated amines being generated from the corresponding methylamine derivative and n-butyl-lithium. Although (1) (R = Me) was

$$cis-[(MeHN)PNBu^{t}]_{2} + 2 Ph_{2}PCl + 2 Et_{3}N \longrightarrow$$

$$(1) (R = Me) + 2Et_{3}NHCl \quad (i)$$

$$cis-[(MeLiN)PNBu^{t}]_{2} + 2 Ph_{2}PCl \longrightarrow$$

$$(1) (R = Me) + 2 LiCl \quad (ii)$$

$$cis-(ClPNBu^{t})_{2} + 2N(PPh_{2})(Me)(Li) \longrightarrow$$

(1) (R = Me) + 2 LiCl (*iii*)

detected in variable amounts from all three reactions, only route (iii), using benzene solution, gave good yields (ca. 60%). This derivative was formed as a ca. 1:1 mixture of isomers which were readily separated by fractional crystallisation. Mass spectroscopic data showed that both isomers had a molecular weight corresponding to the structure shown for (1) (R = Me). This was confirmed by ³¹P n.m.r. (see below), and, for the cis isomer, by X-ray crystallography.¹⁴ The synthesis of the analogous ethyl derivative (1) (R = Et), again as a mixture of geometrical isomers, was carried out similarly. Although (1) $(R = Pr^{i} \text{ and } Bu^{t})$ were also obtained in good yields, only one isomer was obtained in each case; the ³¹P resonance of the endocyclic phosphorus nuclei at ~ 100 p.p.m. indicated that the cisconfiguration was adopted in both cases. Attempted synthesis of a mono(diphenylphosphinoethylamino)derivative, (Ph₂P)EtNP(NBu^t)₂PCl, gave an oily material with the type of ³¹P n.m.r. spectrum expected, but its isolation in a pure state was not achieved.

In the case of compounds (1) (R = Me and Et) good evidence for the cyclodiphosph(III)azane structure (1) in solution was obtained by ³¹P n.m.r. spectroscopy (Table 1). The isomers with the highest field *endo*-P signals ($\delta_{\rm P}$ +112—117 p.p.m.) were assigned *cis* structures (*cf.* ref. 8). The ³¹P n.m.r. spectra constituted samples

| Compound (1) | θ _c /°C | S(P-endo) | $\delta(PPh_{\bullet})$ | J(PNP) endo/Hz | J(PNP) exo/Hz | |
|---|--------------------|----------------|-------------------------|--------------------|-------------------|--|
| cis (R = Me) b | ambient | 116 7 | 49.8 | 19.9 | 356 4 | |
| trans $(\mathbf{R} - \mathbf{M}\mathbf{e})^{b}$ | ambient | 205.8 | 47 7 | 12.2 | 257 6 | |
| $cis (\mathbf{R} - \mathbf{F}t)^d$ | ambient | 114.0 | 45.0 | 15.6 | ca 240 | |
| $t_{\text{rans}} (\mathbf{R} - \mathbf{E}t)$ | ambient | 907.0 | 40.0 | | <i>cu.</i> 349 | |
| $rans (\mathbf{R} = \mathbf{E}t)^{-1}$ | andent | 207.0 | 44.0 | 11.0 | <i>ca.</i> 383 | |
| $cis(\mathbf{R} = \mathbf{Et})^{*}$ | -65 | 112.7 | 46.9 | 11.8 | 415.4 4 | |
| trans ($\mathbf{R} = \mathbf{Et}$) ^a | -60 | 204.3 | 42.8 | 14.2 | 398.7 ° | |
| cis ($\mathbf{R} = \mathbf{Pr^i}$) f | ambient | 104.8 | 33.1 | broad singlets | | |
| cis (R = Pr ⁱ) | 65 | (102.9 | 30.2 | 11.0 | 8.4 | |
| | | 1101.3 | 32.5 | 9.20 | 15.4 | |
| | -110 | (101.9 | 28 2 4 | 81 | 35 1 | |
| $cis (\mathbf{R} = \mathbf{Pr}^{i})$ | | 1 99 8 | 32.5 | 954 | 14 4 | |
| $cis (\mathbf{R} - \mathbf{Bu}^{t})$ | ambient | 1911 | 34.6 | broad singlets | | |
| $ric (\mathbf{R} - \mathbf{D}\mathbf{u})$ | | 101 5 | 95.0 | bioau singlets | | |
| \mathcal{U}_{3} (R = Du) | +00 | 121.0 | 30.7 | | 14 • | |
| $cis (R = Bu^{*}) (77\%)$ | -60 | 119.3 | 31.5 | | 11.0 • | |
| $air (\mathbf{P} - \mathbf{Put}) (990/)$ | - 60 | <i>{</i> 121.4 | 56.1 | 8.6 | 551.8 | |
| $u_{3}(\mathbf{R} = \mathbf{D}\mathbf{u})(25\%)$ | | ો 118.0 | 35.6 | | 17.8 | |
| Bu^{t} | | | | | | |
| N | ambient | 190.1 | 40 0 | 22 9 1 | 389 6 | |
| YP/ DCI | ambient | (PC 1) | 40.0 | 00.4 - | 382.0 | |
| AF FUI | | | | | | |
| IN A | | 139.8 | | | | |
| Bu ^t | | | | | | |

 TABLE 1

 Phosphorus-31 n.m.r. data ^a for [(Ph₂P)RNPNBu^t]₂

 $\begin{bmatrix} Bu^t \\ [X = NEt(PPh_2)] \end{bmatrix}$

^a Shifts are downfield from external 85% H₃PO₄; ambient temperature = ca. 25 °C. The signs of some couplings are known (see text). ^bC₆D₆ solution. ^c J(PNPNP) = -0.5 Hz. ^d CDCl₃ solution. The spectra are broad ($W_4 < 26$ Hz) at ambient temperature. ^c J(PNPNP) = -0.6, |J(PNPNPP)| = 2.4 Hz. ^f [²H₈]toluene-dichloromethane (4:1) solution. ^e $|J(P_{exo} \cdots P_{exo})|$. ^a There is an additional doublet with δ 25.5 p.p.m., $|J(PNP)|_{exo}$ 33.9 Hz (see text). ⁱ |J(PNP) + J(PNPNP)|. ^j J(PNPNP) < 1 Hz.

of AA'XX' spin systems which were readily analysed and simulated. Monomeric phosph(III)azenes of the type $(Ph_2P)RNP=NBu^t$ would simply have given an AX spin system, and the spectrum of a trimer or higher homologue would probably not be able to be simulated in terms of an AA'XX' spin system.

In considering the preferred conformations adopted by the *exo*-PNP skeletons of compounds (1), we have assumed that the *exo*-nitrogen atoms have a planar distribution of bonds, and that nitrogen and phosphorus lone pairs adopt an orthogonal relationship (the nitrogen lone pair is assumed to be located in a p-orbital whose axis is perpendicular to the plane containing the bonds to nitrogen). These assumptions are consistent with most structural studies (*cf.* ref. 12), particularly by X-ray crystallography. These constraints are accommodated by conformations analogous to (2) and (3), for which



large positive (ca. 250—800 Hz) and small negative (ca. -15 to -35 Hz) PNP couplings may be expected.^{12,15} A third conformation in which both phosphorus lone pairs have a *cis*-relationship to the third nitrogen substituent is excluded on steric grounds. The Scheme shows diagrammatically all possible ways in which these conformations can arise in *cis* isomers of (1). An analogous set of conformations can, of course, be drawn for the *trans* isomers.

Both *cis* and *trans* isomers of (1) ($\mathbf{R} = \mathbf{Me}$ and Et) have large couplings, $J(\mathbf{AX})$, which can be assigned (Table 1) to $J(\mathbf{PNP})(\mathbf{exo})$ in a preferred conformation of

type (2). As expected,^{12,15} this coupling increases (by <1 Hz/°C) as the temperature is lowered, whereby the population of conformers analogous to (3) is reduced.



SCHEME Diagrammatic representation of the possible conformations of cis-(1) (R = alkyl) viewed in the best plane containing the P_2N_2 ring. Nitrogen atoms, phenyl-, and R-groups are omitted in the interests of clarity

With (1) (R = Me), the effect of temperature on J(PNP)-(exo) was very small, this being insignificant in the cis isomer. The smaller $P \cdots P$ coupling, J(AA') (ca. 10 Hz), can, in view of previous work,¹⁶ be assigned to J(PNP)(endo). The sign of this coupling may be different in *cis* and *trans* isomers of cyclodiphosph(III)azanes, but analysis of the spectrum does not give any information on this. It proved necessary to include a small negative four-bond coupling, J(PNPNP), to simulate the ³¹P spectra of (1) (R = Me and Et) accurately (Table 1). The N-methyl proton signals of both isomers of (1) (R = Me) (Table 2) comprised a similarity of the ³¹P spectra of isomers of (1) (R = Me) and (1) (R = Et) indicates that the latter isomers also adopt the same type of preferred conformation.

The ³¹P spectrum of *cis*-(1) (R = Prⁱ) in $[{}^{2}H_{8}]$ toluenedichloromethane (4 : 1) solution at room temperature consisted of two broadened singlets (Figure). The absence of signals at low field ($\delta_{p} > 200$ p.p.m.) excludes

| | | TABLE 2 | | |
|--------------------------------------|---------------|--------------------------------------|-------------------------|----------------|
| | Proton n.: | m.r. data ^a for compounds | s (1) | |
| Compound (1) | $\delta(NCH)$ | J(PNCH)/Hz | δ(NCCH) | J(PNCCH) /Hz |
| cis ($\mathbf{R} = \mathbf{Me}$) | 2.78 | +2.6 (endo P) b +2.6 | 1.23 | < 0.3 |
| trans ($R = Me$) | 2.83 | +2.3 (endo P) ^b +2.3 | 1.00 | 0.8 |
| cis (R = Et) | 2.59 | • - | 1.37 (Bu ^t) | < 0.5 |
| | | | 0.71 (Et) | < 0.5 |
| trans ($\mathbf{R} = \mathbf{Et}$) | 2.50 | | 1.08 (Bu ^t) | 0.5 |
| | | | 0.79 (Et) | <0.5 |
| cis (R = Pr ⁱ) | 4.7 (br) | | $1.06 (Bu^{t})$ | ca. 0.3 (endo) |
| · · · · | ζ, | | 1.23 (Pr ⁱ) | |
| cis (R = Bu ^t) | | | 1.52 ` ′ | ca. 0.3 (endo) |
| | | | 1.39 | < 0.3 |

^a CDCl₃ solutions at ambient temperatures. ^b J(PNCH) + J(PNPNCH).

quintet, rather than a doublet of doublets, no doubt due to the magnetic inequivalence of the endo ³¹P nuclei and the large exo-PNP coupling. Some ¹H-{³¹P} double resonance experiments showed that both J(PNCH)couplings are ca. 2—3 Hz and that J(PNCH) and J(PNP)(exo) have the same sign [J(PNPNCH) is assumed to be <1 Hz]. The large exo-PNP spin couplings are therefore ¹³ positive, and the magnitude of J(PNCH) is that expected ¹³ for conformer (a) (and its analogous trans form). This conclusion is supported by the solid state structure of cis-(1) (R = Me).¹⁴ The the possibility that a monomeric species, $(Ph_2P)Pr^iNP=$ NBu^t, might be present. On cooling the solution the spectrum sharpened and at -65 °C four multiplets were apparent (*ca.* 1 : 1 : 1 : 1, see Figure). Low temperature ³¹P spectra obtained at 145.8 MHz confirmed that there were four chemically shifted multiplets. Two of the multiplets (δ_p 32.5 and 101.3) appeared as doublets of doublets whereas the other two (δ_p 30.2 and 102.9) appeared as broader triplets. On cooling further, the latter pair became broader and then sharper, and at -110 °C were doublets of doublets with an additional



The ³¹P n.m.r. spectra of (1) ($R = Pr^i$) in [²H_a]toluene-dichloromethane (4:1) solution at the temperatures indicated. The signals marked X arise from impurities, and possibly other minor conformers. Spectra at different temperatures are offset by 400 Hz

doublet of lower intensity (ca. 25%) at δ_p 25.5 p.p.m. The splittings and asymmetry of the signals observed at -65 °C show that the spectrum is of a four spin ABXY type, rather than two independent AA'XX' systems. The spin couplings are given in Table 1, and they require a P(exo) · · · P(exo) coupling of 9.2 Hz.

The spectrum at -65 °C with four inequivalent phosphorus atoms and relatively small (<40 Hz) PNP couplings is only consistent with (d) being the preferred conformer. However the different spin couplings and chemical shifts obtained at -110 °C clearly show that the -65 °C spectrum still represents the average of more than one conformation. The major conformer, presumed to be now ' frozen out,' is of type (d). It is assumed that the low intensity doublet at δ_p 25.5 is only one of four $^{31}\mathrm{P}$ signals from a conformer closely related to (d) and that the other three signals are obscured by those of the major conformer. It is interesting to consider how the spectrum at -65 °C can arise as an average including the parameters at -110 °C. The averages of the -110 °C parameters for one of the PPh_2 groups are δ_p 27.7 p.p.m. [= 0.8 (28.2) + 0.2 (25.5)] and J(PNP) -34.9 Hz [= 0.8 (-35.1) + 0.2(-33.9)] whereas the observed parameters at -65 °C are δ_p 30.2 p.p.m. and |J(PNP)| 8.4 Hz. Therefore a third conformer with a lower field chemical shift and a large positive J(PNP) must be present. A PNP unit of type (2) satisfies these requirements and if present as conformer (c) in a small amount, its spectrum could still be broad and unobservable at -110 °C. The parameters of the --65 °C spectrum can then be reproduced by inclusion of 10% of a conformer with δ_p 53.1 p.p.m., J(PNP) + 397.7 Hz for one of the PPh₂ groups, cf. (1) (R = Me or Et). The 8.4 Hz coupling at -65 °C is then positive; it is not possible to find a proportion of the third conformer with a reasonable shift and coupling that would make this coupling negative.

The appearance of two sets of signals both consistent with conformer (d) is interesting. It has been proposed (cf. ref. 17) that rotation about N-Prⁱ bonds in which the isopropyl group is sterically crowded may be slow on the n.m.r. time scale even at -60 °C. Two possible arrangements of these groups in conformer (d) are shown in (4) and (5). A conformer analogous to (4) is found in the solid state structure ¹² of (Ph₂P)PrⁱNPPh₂, and (4) is presumably preferred in this case. The coupling between the *exo* ³¹P nuclei is unusual; in (4) it would occur along a 'W' path where one arm of the 'W' is through-space. Related through-space couplings have been inferred from the ¹H and ¹⁹F n.m.r. spectra of other compounds.¹⁸

The ³¹P n.m.r. spectrum of (1) (R = Prⁱ) is solvent dependent; in deuteriochloroform solution at ambient temperature it consists of two broad doublets $[|J(PNP)-(exo) + J(PNPNP)| \sim 26 \text{ Hz}]$ rather than two broadened singlets, presumably due to minor differences in conformational equilibria. The behaviour of the spectra at temperatures down to -60 °C is generally closely related to, but not as clear cut as, that described above. The ambient temperature ³¹P spectrum of cis-(1) (R = Bu^t) consisted of two broadened singlets, the upfield signal being broader. However, at -60 °C, two sets of signals in a ca. 3:1 ratio were apparent, the major component consisting of two triplets with a small splitting (5.5 Hz). This spectrum is readily simulated in terms of an AA'XX' spin system assuming that the spacing of the outer components of the triplets is $\sim J(AX)$, and that $J(AA') + J(XX') \gg J(AX)$. It



is not possible to obtain J(AA') or J(XX') from this spectrum. The conformer giving rise to this spectrum therefore has a mirror plane of symmetry, and an *exo*-PNP skeleton analogous to (3) as in conformers (e) or (f) (Scheme). The ¹³C-{¹H} n.m.r. spectrum of this conformer, also obtained at -60 °C, has an *exo*-

quaternary carbon signal which is a PNBu^tP broadened doublet (separation 25.8 Hz). A ¹³C-{³¹P, ¹H_{noise}} triple resonance experiment showed that this coupling is connected with the endo-P nuclei, so that the t-butyl group and the endo phosphorus lone pair must have 13 a *cis*-relationship, as in conformer (f). Interestingly, the aromatic C^1 and C^2 signals were triplets rather than doublets, even when the endo ³¹P-nuclei are irradiated. The latter experiment means that there must be a significant $P_{exo} \cdots P_{exo}$ coupling (≥ 50 Hz) (C¹ and C² signals form the X part of AA'X spin systems). Attempts to obtain this coupling by a ¹H-{³¹P} double resonance experiment in which the aromatic ortho proton signals were monitored (as in ref. 15) were unsuccessful. The occurrence of a substantial P_{exo} · · · P_{exo} spin coupling is unusual and presumably must be a through space' interaction. This is particularly appropriate to conformation (f), because of the proximity of the exo phosphorus lone pairs.

Four different ³¹P signals are observed for the minor conformer, and the spin couplings can be obtained on a first order basis. The *exo-PNP* couplings of 17.8 and 551.8 Hz indicate that this isomer has conformation (b) or (c); the latter would be favoured on steric grounds. The 551.8 Hz *exo-PNP* coupling is exceptionally large for a diphosphinoamine derivative and is consistent with recent observations ¹² that bulkier substituents on nitrogen produce larger positive *PNP* couplings in conformers analogous to (2).

There is evidence that some diphosphinoamines tend to isomerise to phosph(v)azenes,¹⁹ particularly when bulky P- and N-substituents are present. If this occurred with (1) ($\mathbf{R} = \mathbf{Bu}^t$) the partial structures would be Ph₂-($\mathbf{Bu}^t\mathbf{N}=$)P-P \leq or Ph₂P-P(=NBu^t) \leq . These can be dismissed because the *endo*-P shift is too far to low field for a phosph(v)azene, and both groupings would be expected to have relatively large $P \cdots P$ couplings of *ca*. 250 Hz. The n.m.r. data show unambiguously that cyclophosph(III)azanes, rather than phosph(III)azenes, are present in all cases, despite the bulk of the P- and Nsubstituents. Indeed, the only evidence yet presented ^{2,5} for cyclophosph(III)azane to phosph(III)azene conversion was obtained from solutions at elevated temperatures. However, the reverse process, phosph(III)azene \rightarrow cyclophosph(III)azane, is well documented.^{1,2}

The remarkable tendency for *cis* isomers of cyclodiphosph(III)azanes to be favoured with increasingly bulky *exo*-substituents has also been noted in other amino-derivatives.^{8,10} Unfortunately, the formation of a powdery material on the surface of crystals of (1)

EXPERIMENTAL

Spectroscopic data were obtained as previously described.¹³ All ³¹P spectra were proton-noise-decoupled. General preparative methods have been reported,⁸ and n-butyl-lithium (3.70 mol dm⁻³ in hexane) was obtained commercially. Literature methods were used for the synthesis of 2-cis-4-dichloro-1,3-di-t-butylcyclodiphosph(III)azane,²¹ and of diphenylphosphinoamines, NRH(PPh₂) (R = Me, Et, Prⁱ, or Bu^t).¹⁵

2-cis-4(and 2-trans-4)-Bis(diphenylphosphinomethylamino)-1,3-di-t-butylcyclodiphosph(III)azane (1) (R = Me).— Butyl-lithium (18 mmol) was added to diphenylphosphinomethylamine (3.9 g, 18 mmol) in benzene (100 cm³) in a dropping funnel. The mixture was occasionally agitated (0.5 h) and then added to a stirred solution of 2,4-dichloro-

| | | Carbon-I | 3 n.m.r. da | ta ^a for compo | unds (1) | | | |
|--|------------------------------|-------------------------------|------------------------------|---|------------------------------------|---|--------------------------------|-----------------|
| | Endo | | | | Exo b | | | |
| Compound (1) cis (R = Me) trans (R = Me) | δ(NC) ° 52.3 50.8 | J(PNC) / Hz 15.2 5.9 | δ(NCC) 31.1 30.2 | <i>J</i> (<i>P</i> NC <i>C</i>) / Hz 6.9 5.3 | δ(NC) 28.6 28.4 | J(PNC) / Hz ca. 8.4 11.0, 8.2 | δ(NCC) | J(PNCC) Hz |
| cis (R = Et) trans (R = Et) $cis (R = Pr^{i})$ $cis (R = Bu^{t})$ | 53.3 50.9 53.1 54.4 | 16.5 5.9 16.4 19.2 | 31.1 30.8 31.7 32.5 | 7.7 5.0 7.3 8.7 | 39.0 39.8 ca. 44.7 d 64.0 | ca. 5 5.6 25.8 | $18.5 \\ 16.5 \\ 24.8 \\ 34.3$ | 14.0 ° |

TABLE 3

^a In CDCl₃ solution at ambient temperature. ^b PNC couplings not distinguished except when $R = Bu^{t}$ (see text). Aromatic carbon signals $\delta_{C^{1}}$ 138.5, $J(PC^{1})$ 16; $\delta_{C^{2}}$ 133.3; $J(PCC^{2})$ 22 Hz, $\delta_{C^{0}C^{1}}$ ca. 128, 129 p.p.m., except when $R = Bu^{t}$ (see below). ^c Relative to internal SiMe₄. ^d At -40 °C. ^e Values $\delta_{C^{1}}$ 141.8, $J(PC^{1})$ 32.1; $\delta_{C^{1}}$ 132.5 p.p.m., $J(PC^{2})$ 23.1 Hz; C¹ and C² signals are triplets, the spacing of the outer components being $J(PC^{2} \text{ or } C^{1})$.

 $(R = Bu^t)$ has so far precluded its study by X-ray crystallography. It is worth noting that attempts¹² to prepare the diphosphinoamine, NBu^t(PPh₂)₂, led to the isolation of Ph₂PP(O)Ph₂, suggesting the intermediate formation of Ph₂PP(=NBu^t)Ph₂. The cyclodiphosph(III)azane ring in (1) (R = Bu^t) therefore appears to be more effective than the diphenylphosphinogroup in stabilising the diphosphinoamine structure. Compound (1) (R = Bu^t) might also be stabilised by an interaction between the *exo*-phosphorus lone pairs (*cf.* ref. 20).

Our assignments of the preferred conformations for the *exo*-PNP skeletons (Scheme) of the cyclodiphosph(III)-azanes (1) are summarised below.

Compound (1) Isomer Preferred conformation (a)(a) (a) (a) $\mathbf{R} = \mathbf{M}\mathbf{e}$ cis $\mathbf{R} = \mathbf{M}\mathbf{e}$ trans $\mathbf{R} = \mathbf{E}\mathbf{t}$ cis $\mathbf{R} = \mathbf{E}\mathbf{t}$ trans (d) [with (c) also occurring] (f) [with (c) also occurring] $\mathbf{R} = \mathbf{P}\mathbf{r}^{\mathbf{i}}$ cis $R = Bu^t$ cis

As in the diphosphinoamines, $NR'(PPh_2)_2$ (R' = alkyl),¹² P-N-P conformations of type (3) become favoured over type (2) with increasingly bulky *N*-alkyl groups. However, the occurrence of a conformation of type (2) [conformer (c)] in (1) ($R = Bu^t$) also emphasises the importance of the phosphorus, as well as the nitrogen substituents in determining the preferred conformation.

1,3-di-t-butylcyclodiphosph(III)azane (2.6 g, 9.5 mmol) in benzene (25 cm³). The product was boiled under reflux (2 h) and left to cool. The precipitates of lithium chloride and benzene were removed to leave a brown solid which was dissolved in a hot pentane-methylene chloride mixture (ca. 4:1). The first batch of crystals obtained on cooling were further recrystallised from the same solvent mixture leaving *trans*-(1) (R = Me) (1.7 g, 28%), m.p. 190-192 °C (Found: C, 64.4; H, 7.0; N, 8.9; *m/e* 636. C₃₄H₄₄N₄P₄ requires C, 64.6; H, 7.0; N, 8.9%; *m/e* 632). A second batch of crystals was similarly recrystallised to give cis-(1) (R = Me) (1.9 g, 32%), m.p. 170-173 °C (Found: C, 64.7; H, 7.0; N, 8.7%; *m/e* 636). Other synthetic routes to these isomers were investigated as described in the Results section.

2-trans-4 (and 2-cis-4)-Bis(diphenylphosphinoethylamino)-1,3-di-t-butylcyclodiphosph(111)azane (1) (R = Et).—These compounds were obtained similarly. Compound trans-(1) (R = Et) (29%), m.p. 188—191 °C (Found: C, 66.3; H, 7.6; N, 7.4; m/e 660. C₃₆H₄₈N₄P₄ requires C, 65.5; H, 7.3; N, 8.5%; m/e 660) and cis-(1) (R = Et) (15%), m.p. 140—142 °C (Found: C, 65.7; H, 7.4; N, 8.4%; m/e 660).

2-cis-4-Bis(diphenylphosphinoisopropylamino)-1,3-di-tbutylcyclodiphosph(III)azane (1) ($R = Pr^i$).—n-Butyllithium (17.3 mmol) in hexane was mixed with diphenylphosphinoisopropylamine (4.2 g, 17.3 mmol) in benzene (25 cm³), agitated (0.25 h), and added dropwise to a stirred solution of 2-cis-4-dichloro-1,3-di-t-butylcyclodiphosph(III)azane (2.4 g, 8.6 mmol) in benzene (25 cm³). The mixture was boiled under reflux (3 h) and the lithium chloride and solvent removed leaving a brownish crystalline solid. Recrystallisation from light petroleum (b.p. 40—60 °C)methylene chloride (1:1) gave cis-(1) ($R = Pr^i$) (2.6 g, 44%), m.p. 184-186 °C (Found: C, 66.4; H, 7.8; N, 8.4; m/e 688. C₃₈H₅₂N₄P₄ requires C, 66.3; H, 7.6; N, 8.1%; m/e 688). This compound formed a mixture of products (³¹P n.m.r.) on standing at ambient temperature over a period of one year. All the other compounds (1) appeared to be stable under these conditions.

2-cis-4-Bis(diphenylphosphino-t-butylamino)-1,3-di-t-

butylcyclodiphosph(III)azane (1) (R = Bu^t).—This compound was prepared similarly using diphenylphosphino-tbutylamine. Recrystallisation from light petroleum (b.p. 40-60 °C) gave (1) (R = Bu^t) (56%), m.p. 155-158 °C (Found: C, 67.2; H, 7.7; N, 7.7. C₄₀H₅₆N₄P₄ requires C, 67.0; H, 7.8; N, 7.8%).

2-Chloro-cis-4-(diphenylphosphinoethylamino)-1,3-di-tbutylcyclodiphosph(III)azane.-Reaction of lithiated diphenylphosphinoethylamine (23 mmol) with 2-cis-4-dichloro-1,3-di-t-butylcyclodiphosph(III)azane (23 mmol) under the same conditions as in the preparation of (1) (R =Me) gave an oily product which could not be purified by crystallisation. Phosphorus n.m.r. spectroscopy (Table 1) indicated that the compound constituted >70% of the product.

We thank Mr. D. A. Harvey for some preliminary experiments, and Dr. I. H. Sadler (University of Edinburgh) for the 145.8 MHz ³¹P n.m.r. spectra, obtained on a Bruker WH360 spectrometer.

[1/1990 Received, 30th December, 1981]

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