Synthesis and Conformational Studies of (Diphenylphosphinoamino)-cyclodiphosph(III)azanes

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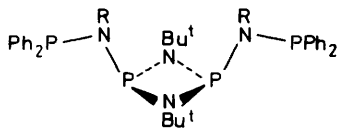
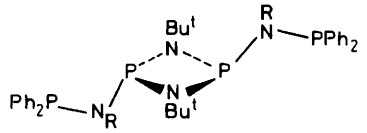
A series of 2,4-bis(diphenylphosphinoalkylamino)-1,3-di-t-butylcyclodiphosph(III)azanes, $[(Ph_2P)RNPNBu^t]_2$ [R = Me or Et (*cis*- and *trans*-isomers); R = Pr^i or Bu^t (*cis*-isomers)], have been prepared by the reactions of *N*-lithiated alkyl-*N*-(diphenylphosphino)amines, $N(PPh_2)(R)(Li)$, with 2-*cis*-4-dichloro-1,3-di-t-butylcyclodiphosph(III)azane, $(ClPNBu^t)_2$, in benzene solution. Hydrogen-1, ^{13}C, and ^{31}P n.m.r. spectroscopy show that these compounds are cyclodiphosph(III)azanes rather than phosph(III)azenes, $(Ph_2P)RNP{=}NBu^t$, in solution, and variable temperature ^{31}P n.m.r. data have enabled the preferred conformations of the *exo*-P–N–P skeletons to be identified. In the case of $[(Ph_2P)RNPNBu^t]_2$ (R = Pr^i 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 $SiMe_3$),[1,2] R''P=NBu^t (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 $SiMe_3$; 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 diphenylphosphinoamino-substituted cyclodiphosp(III)azanes, (1) (R = alkyl), in which the possibility of phosph(III)azene formation is



cis

(1)



trans

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 conformations 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

$$cis\text{-}[(MeHN)PNBu^t]_2 + 2\ Ph_2PCl + 2\ Et_3N \longrightarrow (1)\ (R = Me) + 2Et_3NHCl \quad (i)$$

$$cis\text{-}[(MeLiN)PNBu^t]_2 + 2\ Ph_2PCl \longrightarrow (1)\ (R = Me) + 2\ LiCl \quad (ii)$$

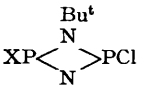
$$cis\text{-}(ClPNBu^t)_2 + 2N(PPh_2)(Me)(Li) \longrightarrow (1)\ (R = Me) + 2\ LiCl \quad (iii)$$

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 ^{31}P 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 and Bu^t) were also obtained in good yields, only one isomer was obtained in each case; the ^{31}P resonance of the endocyclic phosphorus nuclei at ~100 p.p.m. indicated that the *cis*-configuration was adopted in both cases. Attempted synthesis of a mono(diphenylphosphinoethylamino)-derivative, $(Ph_2P)EtNP(NBu^t)_2PCl$, gave an oily material with the type of ^{31}P 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 ^{31}P n.m.r. spectroscopy (Table 1). The isomers with the highest field *endo*-P signals (δ_P +112—117 p.p.m.) were assigned *cis* structures (*cf.* ref. 8). The ^{31}P n.m.r. spectra constituted samples

TABLE 1

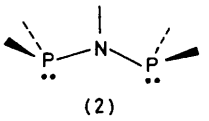
Phosphorus-31 n.m.r. data [a] for $[(Ph_2P)RNPNBu^t]_2$

Compound (1)	θ_c/°C	δ(*P-endo*)	δ(PPh_2)	|*J*(*PNP*)| *endo*/Hz	|*J*(*PNP*)| *exo*/Hz
cis (R = Me) [b]	ambient	116.7	49.8	12.2	356 [c]
trans (R = Me) [b]	ambient	205.8	47.7	13.8	357 [c]
cis (R = Et) [d]	ambient	114.0	45.0		*ca.* 349
trans (R = Et) [d]	ambient	207.0	44.6		*ca.* 383
cis (R = Et) [d]	−65	112.7	46.9	11.8	415.4 [e]
trans (R = Et) [d]	−60	204.3	42.8	14.2	398.7 [e]
cis (R = Pr^i) [f]	ambient	104.8	33.1	broad singlets	
cis (R = Pr^i)	−65	102.9	30.2	11.0	8.4
		101.3	32.5	9.2 [g]	15.4
cis (R = Pr^i)	−110	101.9	28.2 [h]	8.1	35.1
		99.8	32.5	9.5 [g]	14.4
cis (R = Bu^t)	ambient	121.1	34.6	broad singlets	
cis (R = Bu^t)	+60	121.5	35.7		14 [i]
cis (R = Bu^t) (77%)	−60	119.3	31.5		11.0 [i]
cis (R = Bu^t) (23%)	−60	121.4	56.1		551.8
		118.0	35.6	8.6	17.8
 [X = NEt(PPh_2)]	ambient	190.1 (*P*Cl) 139.8	49.9	33.2 [j]	382.6

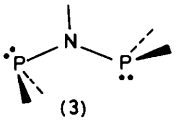
[a] Shifts are downfield from external 85% H_3PO_4; ambient temperature = *ca.* 25 °C. The signs of some couplings are known (see text). [b] C_6D_6 solution. [c] *J*(*PNPNP*) = −0.5 Hz. [d] $CDCl_3$ solution. The spectra are broad ($W_{\frac{1}{2}}$ < 26 Hz) at ambient temperature. [e] *J*(*PNPNP*) = −0.6, |*J*(*PNPNPNP*)| = 2.4 Hz. [f] [$^2H_8$]toluene–dichloromethane (4 : 1) solution. [g] $|J(P_{exo} \cdots P_{exo})|$. [h] 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



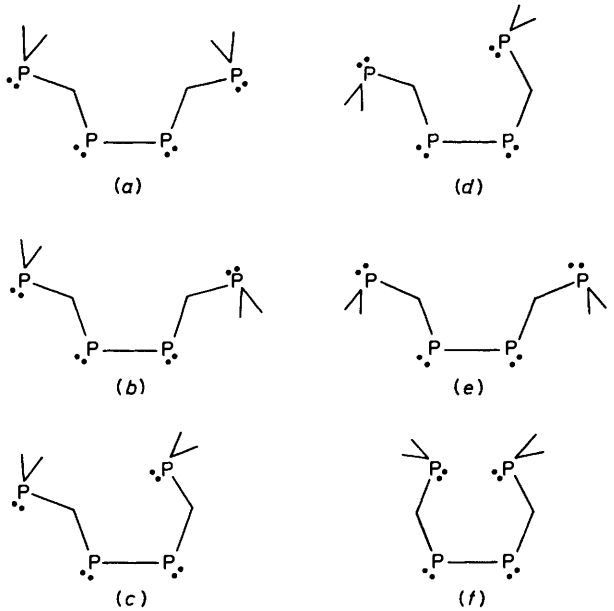
(2)



(3)

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) (R = Me and Et) have large couplings, *J*(AX), which can be assigned (Table 1) to *J*(*PNP*)(*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 · · · 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 ^{31}P 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 quintet, rather than a doublet of doublets, no doubt due to the magnetic inequivalence of the *endo* ^{31}P nuclei and the large *exo*–*PNP* coupling. Some ^{1}H-$\{^{31}P\}$ 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 similarity of the ^{31}P spectra of isomers of (1) (R = Me) and (1) (R = Et) indicates that the latter isomers also adopt the same type of preferred conformation.

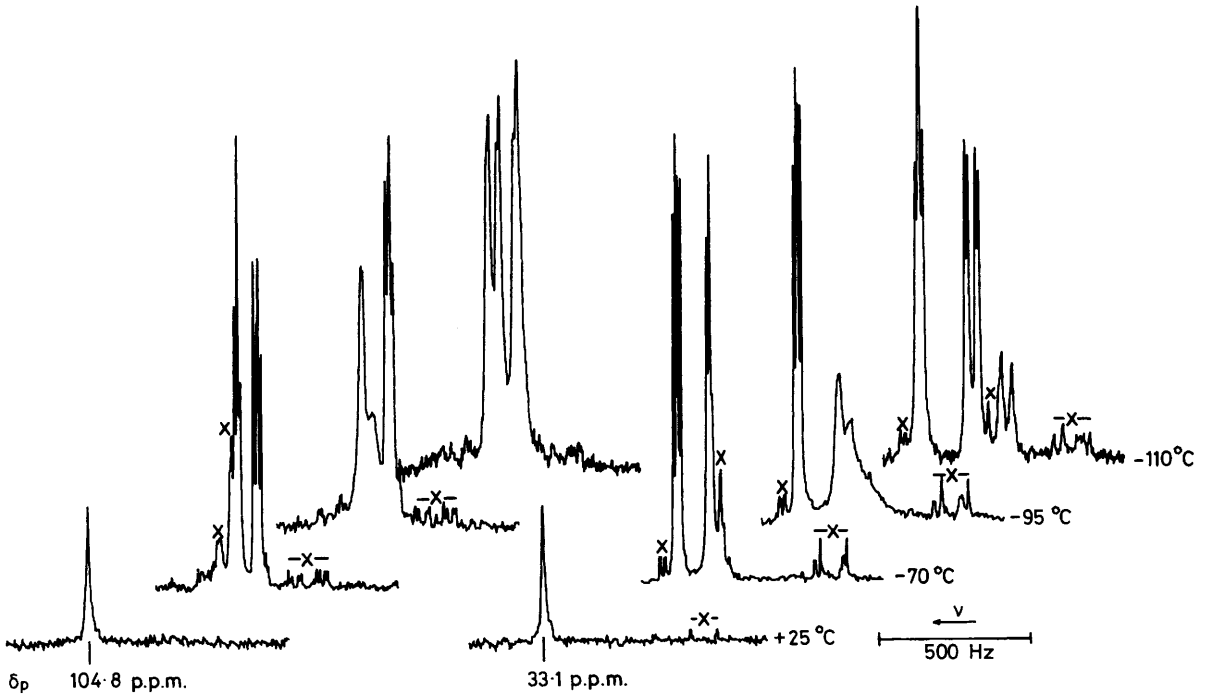
The ^{31}P spectrum of *cis*-(1) (R = Pr^i) in [$^2H_8$]toluene–dichloromethane (4 : 1) solution at room temperature consisted of two broadened singlets (Figure). The absence of signals at low field (δ_P >200 p.p.m.) excludes the possibility that a monomeric species, $(Ph_2P)Pr^iNP{=}NBu^t$, might be 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 ^{31}P 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

TABLE 2

Proton n.m.r. data [a] for compounds (1)

Compound (1)	δ(NC*H*)	*J*(*P*NC*H*)/Hz	δ(NCC*H*)	|*J*(*P*NCC*H*)|/Hz
cis (R = 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) 0.71 (Et)	<0.5 <0.5
trans (R = Et)	2.50		1.08 (Bu^t) 0.79 (Et)	0.5 <0.5
cis (R = Pr^i)	4.7 (br)		1.06 (Bu^t) 1.23 (Pr^i)	*ca.* 0.3 (*endo*)
cis (R = Bu^t)			1.52 1.39	*ca.* 0.3 (*endo*) <0.3

[a] $CDCl_3$ solutions at ambient temperatures. [b] $J(PNCH) + J(PNPNCH)$.



The ^{31}P n.m.r. spectra of (1) (R = Pr^i) in [$^2H_8$]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

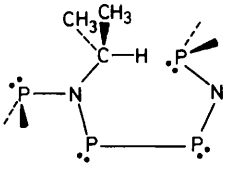
doublet of lower intensity (*ca.* 25%) at δ_P 25.5 p.p.m. The splittings and asymmetry of the signals observed at −65 °C show that the spectrum is of a four spin ABXY type, rather than two independent AA'XX' systems. The spin couplings are given in Table 1, and they require a P(*exo*) · · · P(*exo*) 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}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 PPh_2 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–Pr^i 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 $(Ph_2P)Pr^iNPPh_2$, and (4) is presumably preferred in this case. The coupling between the *exo* ^{31}P 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 ^{1}H and ^{19}F n.m.r. spectra of other compounds.[18]

The ^{31}P n.m.r. spectrum of (1) (R = Pr^i) is solvent dependent; in deuteriochloroform solution at ambient temperature it consists of two broad doublets [|*J*(*PNP*)(*exo*) + *J*(*PNPNP*)| ~ 26 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 ^{31}P 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 ~*J*(AX), and that *J*(AA') + *J*(XX') ≫ *J*(AX). It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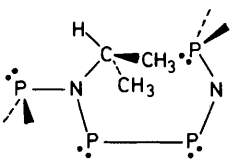
(5)

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 ^{13}C-{^{1}H} n.m.r. spectrum of this conformer, also obtained at −60 °C, has an *exo*-PNBu^{t}P quaternary carbon signal which is a broadened doublet (separation 25.8 Hz). A ^{13}C-{^{31}P, $^1H_{noise}$} 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* ^{31}P-nuclei are irradiated. The latter experiment means that there must be a significant P_{exo} · · · P_{exo} coupling (≳50 Hz) (C^1 and C^2 signals form the X part of AA'X spin systems). Attempts to obtain this coupling by a ^{1}H-{^{31}P} 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 ^{31}P 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) (R = Bu^t) the partial structures would be Ph_2-(Bu^{t}N=)P–P< or Ph_2P–P(=NBu^t)<. 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 · · · 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 N-substituents. 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→ 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) (R = Bu^t) has so far precluded its study by *X*-ray crystallography. It is worth noting that attempts [12] to prepare the diphosphinoamine, $NBu^t(PPh_2)_2$, led to the isolation of $Ph_2PP(O)Ph_2$, suggesting the intermediate formation of $Ph_2PP(=NBu^t)Ph_2$. The cyclodiphosph(III)azane ring in (1) (R = Bu^t) therefore appears to be more effective than the diphenylphosphino-group 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
R = Me	*cis*	(*a*)
R = Me	*trans*	(*a*)
R = Et	*cis*	(*a*)
R = Et	*trans*	(*a*)
R = Pr^i	*cis*	(*d*) [with (*c*) also occurring]
R = Bu^t	*cis*	(*f*) [with (*c*) also occurring]

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.

TABLE 3

Carbon-13 n.m.r. data [a] for compounds (1)

	Endo				*Exo* [b]			
Compound (1)	δ(NC) [c]	|*J*(PNC)|/Hz	δ(NCC)	|*J*(PNCC)|/Hz	δ(NC)	|*J*(PNC)|/Hz	δ(NCC)	|*J*(PNCC)|/Hz
cis (R = Me)	52.3	15.2	31.1	6.9	28.6	*ca.* 8.4		
trans (R = Me)	50.8	5.9	30.2	5.3	28.4	11.0, 8.2		
cis (R = Et)	53.3	16.5	31.1	7.7	39.0	*ca.* 5	18.5	
trans (R = Et)	50.9	5.9	30.8	5.0	39.8	5.6	16.5	
cis (R = Pr^i)	53.1	16.4	31.7	7.3	*ca.* 44.7 [d]		24.8	
cis (R = Bu^t)	54.4	19.2	32.5	8.7	64.0	25.8	34.3	14.0 [e]

[a] In $CDCl_3$ solution at ambient temperature. [b] *PNC* couplings not distinguished except when R = Bu^t (see text). Aromatic carbon signals δ_{C^1} 138.5, $J(PC^1)$ 16; δ_{C^2} 133.3; $J(PCC^2)$ 22 Hz, $\delta_{C^3C^4}$ *ca.* 128, 129 p.p.m., except when R = Bu^t (see below). [c] Relative to internal $SiMe_4$. [d] At −40 °C. [e] Values δ_{C^1} 141.8, $J(PC^1)$ 32.1; δ_{C^2} 132.5 p.p.m., $J(PC^2)$ 23.1 Hz; C^1 and C^2 signals are triplets, the spacing of the outer components being $J(PC^2$ or $C^1)$.

EXPERIMENTAL

Spectroscopic data were obtained as previously described.[13] All ^{31}P 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, $NRH(PPh_2)$ (R = Me, Et, Pr^i, 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 cm^3) in a dropping funnel. The mixture was occasionally agitated (0.5 h) and then added to a stirred solution of 2,4-dichloro-1,3-di-t-butylcyclodiphosph(III)azane (2.6 g, 9.5 mmol) in benzene (25 cm^3). 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. $C_{34}H_{44}N_4P_4$ 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*(III)*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. $C_{36}H_{48}N_4P_4$ 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-t-butylcyclodiphosph*(III)*azane* (1) (R = Pr^i).—n-Butyl-lithium (17.3 mmol) in hexane was mixed with diphenylphosphinoisopropylamine (4.2 g, 17.3 mmol) in benzene (25 cm^3), 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 cm^3). 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. $C_{38}H_{52}N_4P_4$ requires C, 66.3; H, 7.6; N, 8.1%; *m/e* 688). This compound formed a mixture of products (^{31}P 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-t-butylamine. 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. $C_{40}H_{56}N_4P_4$ requires C, 67.0; H, 7.8; N, 7.8%).

2-*Chloro*-cis-4-(*diphenylphosphinoethylamino*)-1,3-*di-t-butylcyclodiphosph*(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.

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