# HEXAALKOXY AND HEXAARYLOXY 1,3,2λ⁵,4λ⁵-DIAZADIPHOSPHETIDINES

S. S. Kumaravel[a]; S. S. Krishnamurthy[a]; Roberta O. Day[b]; Robert R. Holmes[b]

[a] Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore, India [b] Department of Chemistry, University of Massachusetts, Amherst, MA, U.S.A.

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# HEXAALKOXY AND HEXAARYLOXY $1,3,2\lambda^5,4\lambda^5$-DIAZADIPHOSPHETIDINES

## S. S. KUMARAVEL and S. S. KRISHNAMURTHY

*Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore-560012, India*

and

## ROBERTA O. DAY and ROBERT R. HOLMES

*Department of Chemistry, University of Massachusetts, Amherst, MA 01003 U.S.A.*

The reaction of the hexachlorodiazadiphosphetidine $(MeNPCl_3)_2$ with NaOR (R = $CH_2CF_3$ or $C_6H_5$) yields the hexaalkoxy/aryloxy derivatives $[MeNP(OR)_3]_2$. On the other hand, the reaction of the N-phenyl derivative with $NaOCH_2CF_3$ affords the monophosphazene $PhN\!=\!P(OCH_2CF_3)_3$. Spectroscopic data for the new compounds are presented. The structure of the trifluoroethoxy derivative $[MeNP(OCH_2CF_3)_3]_2$ has been confirmed by a single crystal X-ray diffraction study. It crystallizes in the triclinic space group P$\bar{1}$ with a = 9.024(2) Å, b = 9.255(2) Å, c = 9.944(2) Å, $\alpha$ = 69.68(2)°, $\beta$ = 60.16(2)°, $\gamma$ = 78.88(2)°, and Z = 1. The final conventional unweighted residual is 0.044. The transformation of $[MeNP(OCH_2CF_3)_3]_2$ into its monomer at 110°C and its redistribution reaction with $[MeNPF_3]_2$ have been investigated by NMR spectroscopy. The formation of dimeric species appears to be favored by electron withdrawing groups at phosphorus promoting delocalization in the P—N—P system.

*Key words:* Diazadiphosphetidine; monophosphazene; cyclodiphosphazane; redistribution; pseudorotation; X-ray structure.

## INTRODUCTION

Although alkoxy and amino substituted monomeric phosphazo species such as $MeN\!=\!P(OMe)_3$ and $MeN\!=\!P(NMe_2)_3$ have been prepared by the treatment of $MeN_3$ with $P(OMe)_3$ and $P(NMe_2)_3$ respectively,[1,2] the corresponding cyclic dimers are unknown. The reaction of the cyclodiphosphazane $(PhNPCl_3)_2$ with diethylamine or ethanol gives the monophosphazenes $PhN\!=\!PCl_n(NEt_2)_{3-n}(n = 0,1,2)$[3] or $PhN\!=\!P(OEt)_3$.[4] Phenols also cleave the $P_2N_2$ ring.[5] However, in the reaction of $(MeNPF_3)_2$ with LiOMe, replacement of up to four fluorine atoms can be achieved to obtain $[MeNPF(OMe)_2]_2$.[6] In this paper, we report the isolation of hitherto unprecedented hexa(alkoxy)/(aryloxy)cyclodiphosphazanes from the reaction of $(MeNPCl_3)_2$ with sodium trifluoroethoxide or phenoxide. The dimeric structure of the trifluoroethoxy derivative is confirmed by a single crystal X-ray diffraction study and its redistribution reaction with the hexafluoro derivative $(MeNPF_3)_2$ is investigated by NMR spectroscopy.

## RESULTS AND DISCUSSION

*Synthesis and Spectroscopic Data.* The reactions of hexachloro cyclodiphospha-zanes $(RNPCl_3)_2$ with trifluoroethoxide or phenoxide yield the hexa(alkoxy)/(ar-yloxy) derivatives (2, 3) or the monomeric phosphazene (6) depending on the nature of R as shown in Scheme 1. Compounds 2 and 3 are colorless crystalline solids and their cyclic structure has been established from spectroscopic data (see Experi-mental), in particular their high-field $^{31}P$ chemical shift ($-71.8$ $\delta$ for 2 and $-77.4$ $\delta$ for 3).[13] The monomeric phosphazene 6 exhibits a $^{31}P$ chemical shift of $-16.7$ $\delta$ which may be compared with the values of 14.2, 32.6, and 1.1 $\delta$ for $PhN{=}P(NEt_2)_3$, $MeN{=}P(NMe_2)_3$ and $MeN{=}P(OMe)_3$ respectively.[2,3] The $^1H$ NMR spectrum of 6 does not show virtual coupling for the $OC\underline{H}_2CF_3$ protons in contrast to the behavior of 2. The IR spectrum of 6 shows a band at 1305 cm$^{-1}$ which may be assigned to the P=N stretching vibration.[14]
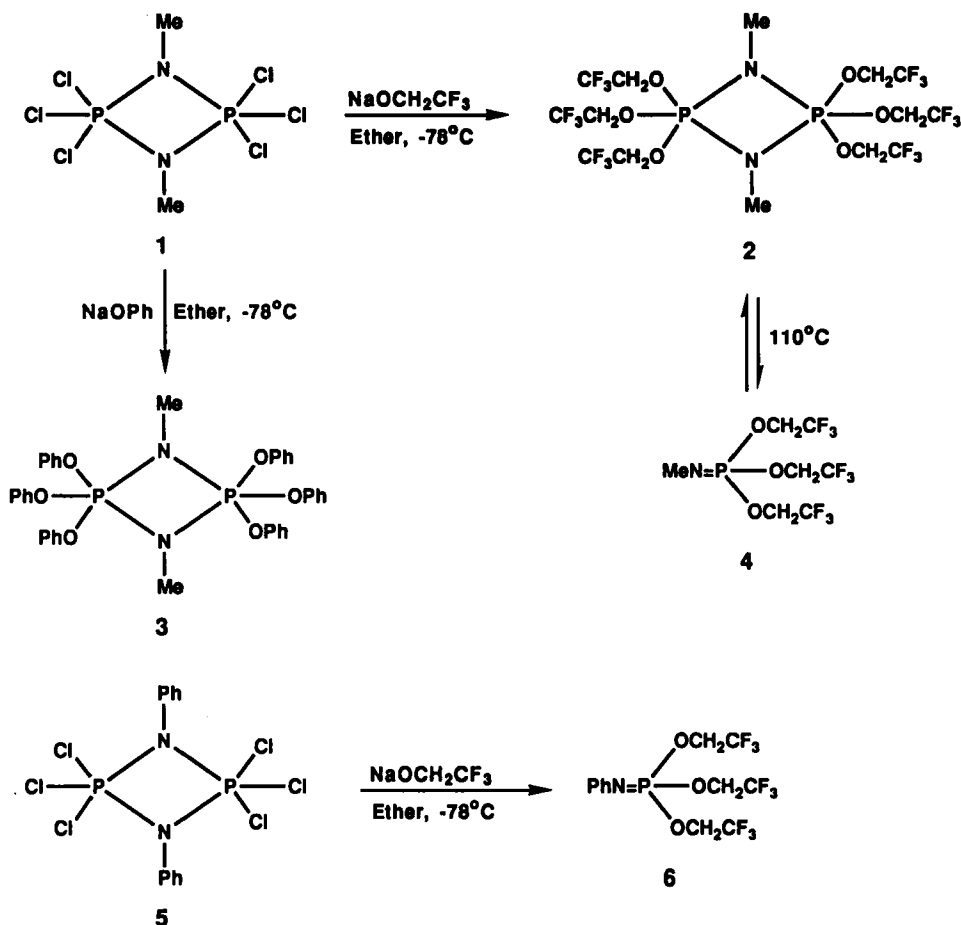


**Scheme 1**

The dimeric structure of **2** has been confirmed by a single crystal X-ray diffraction study as described below.

The $^1$H NMR spectra of **2** and **3** show only a single triplet for NC$\underline{H}_3$ protons even at $-60°C$ although one would anticipate two doublets because of different couplings involving an apical and an equatorial orientation at the two trigonal bipyramidal phosphorus centres. Presumably, P—N bond equilibration[15] is fast on the NMR time scale even at $-60°C$. Harris and coworkers[16] have reported that for the tetraphenyl difluoro derivative (MeNPPh$_2$F)$_2$, two major doublets for N-C$\underline{H}_3$ protons can be observed even at 25°C. The hexakis(trifluoroethoxy) derivative dissociates into the monomeric species MeN=P(OCH$_2$CF$_3$)$_3$ at 110°C as revealed by NMR spectroscopy. In addition to the triplet for dimeric form (**2**) a doublet at 2.80 $\delta$ with a $J_{PH}$ of 24 Hz is seen in the spectrum (Figure 1).[17] This doublet disappears when the sample is cooled to 25°C.

The mass spectrum of [MeNP(OCH$_2$CF$_3$)$_3$]$_2$ (**2**) does not show the molecular ion peak at m/z 714. A peak corresponding to (M—CH$_2$CF$_3$)$^+$ (m/z 615) is observed with a relative intensity of 6.8% with respect to the base peak at m/z 69 attributable to CF$_3^+$. The other major peaks observed are [MeNP(OCH$_2$CF$_3$)$_3$]$^+$ (m/z 357), [MeNP(OCH$_2$CF$_3$)$_2$(OCH$_2$CF$_2$)]$^+$ (m/z 338) and [P(OCH$_2$CF$_3$)$_3$]$^+$ (m/z 328) with relative intensities of 27.8, 17.2 and 21.3%, respectively. The absence of molecular ion peaks in the mass spectra of the hexacyclodiphosphazanes, (Cl$_3$PNR)$_2$ (R=Me or CH$_2$C$_6$H$_5$) has been reported.[18]

*Redistribution Reaction Between Hexa(trifluoroethoxy) and Hexafluoro Cyclodiphosphazanes.* Fluorine atoms and alkoxy groups (OCH$_2$CF$_3$ or OCH$_2$CCl$_3$) redistribute readily around a pentacoordinated phosphorus centre resulting in inter-
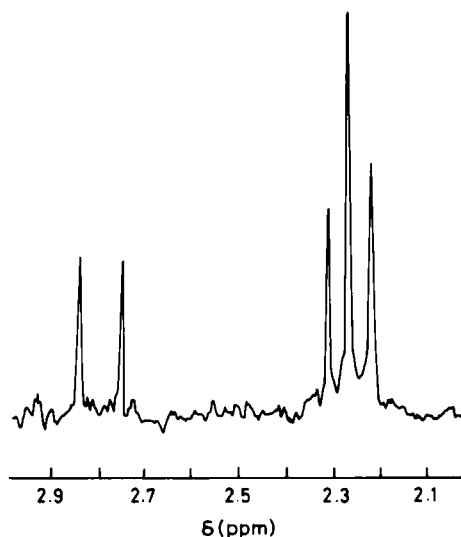


FIGURE 1 $^1$H NMR (270 MHz) spectrum of [(MeN)P(OCH$_2$CF$_3$)$_3$]$_2$ (**2**) at 110°C in C$_6$H$_5$Cl (NMe region only).
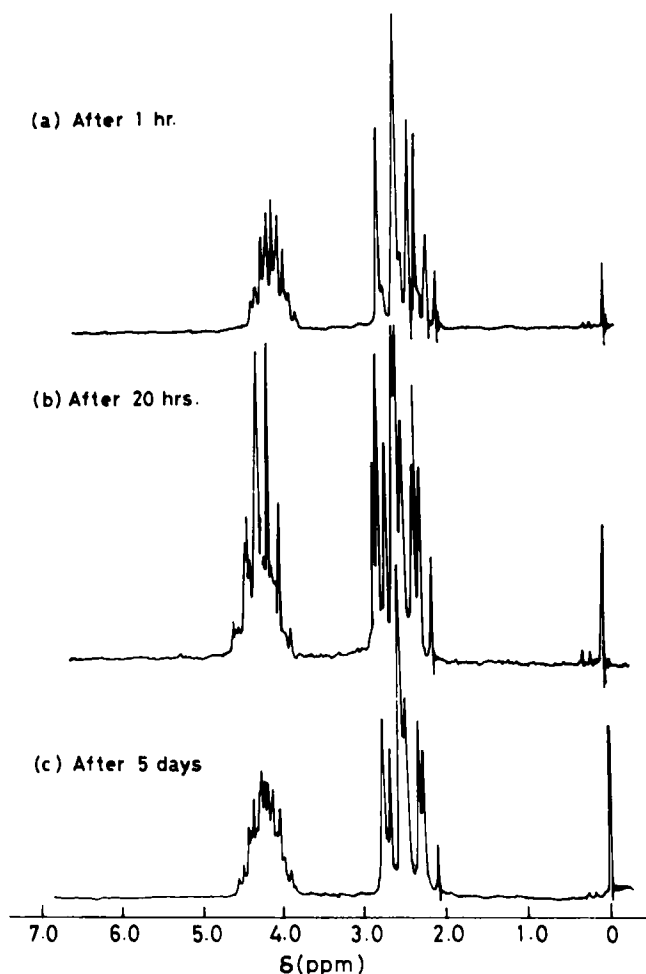
FIGURE 2   $^1$H NMR (60 MHz) spectra of a 2:1 mixture of [(MeN)PF$_3$]$_2$ and [(MeN)P(OCH$_2$CF$_3$)$_3$]$_2$ in CDCl$_3$.

conversions among the series of (alkoxy)-fluorophosphoranes, PhPF$_{4-n}$(OR)$_n$.[19] A measurement of redistribution equilibria can provide a method for evaluating the apicophilicity of the substituents. In the present study, redistribution among (tri-fluoroethoxy) fluoro cyclodiphosphazanes, [(MeN)P]$_2$[(OR)$_{6-n}$F$_n$] (n = 1–6) has been investigated by NMR spectroscopy. Because of the extremely complex $^1$H, $^{19}$F and $^{31}$P spectra of the mixtures, it has been difficult to determine the relative amounts of each of the species and assign the resonances to the individual species. A relatively simple $^1$H NMR spectrum is obtained when (MeNPF$_3$)$_2$ and [MeNP(OCH$_2$CF$_3$)$_3$]$_2$ (**2**) are mixed in a 2:1 molar ratio in CDCl$_3$ and the spectrum recorded at various intervals of time (Figure 2). After 5 days, an equilibrium is reached and the spectrum can be interpreted in terms of the following equilibrium:

*trans* *gauche*
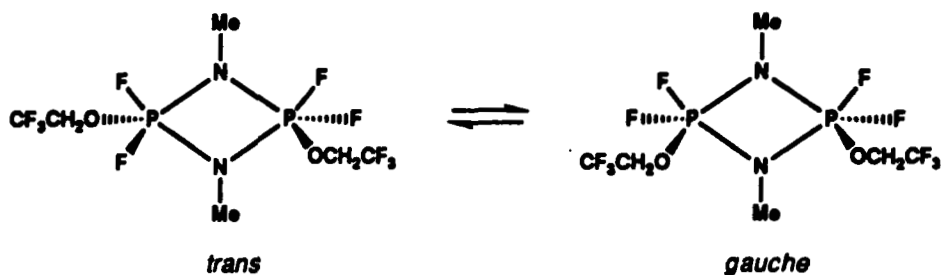
This result is in accord with the supposition that pseudorotation at both the phosphorus centres of cyclodiphosphazanes occurs in a more-or-less concerted fashion[20] and hence cyclodiphosphazanes with symmetrically substituted phosphorus atoms will be favored compared to unsymmetrically substituted cyclodiphosphazanes so that distortions at both the phosphorus centres remain nearly the same. The redistribution reactions of diazadiphosphetidines should be treated in a different manner compared to (alkoxy) fluorophosphoranes where the relative apicophilicity of the substituents mainly govern the redistribution equilibria.

*Crystal and Molecular Structure of [MeNP(OCH$_2$CF$_3$)$_3$]$_2$ (2).* The molecular geometry and atom labeling scheme for **2** is given in the ORTEP plot of Figure 3.
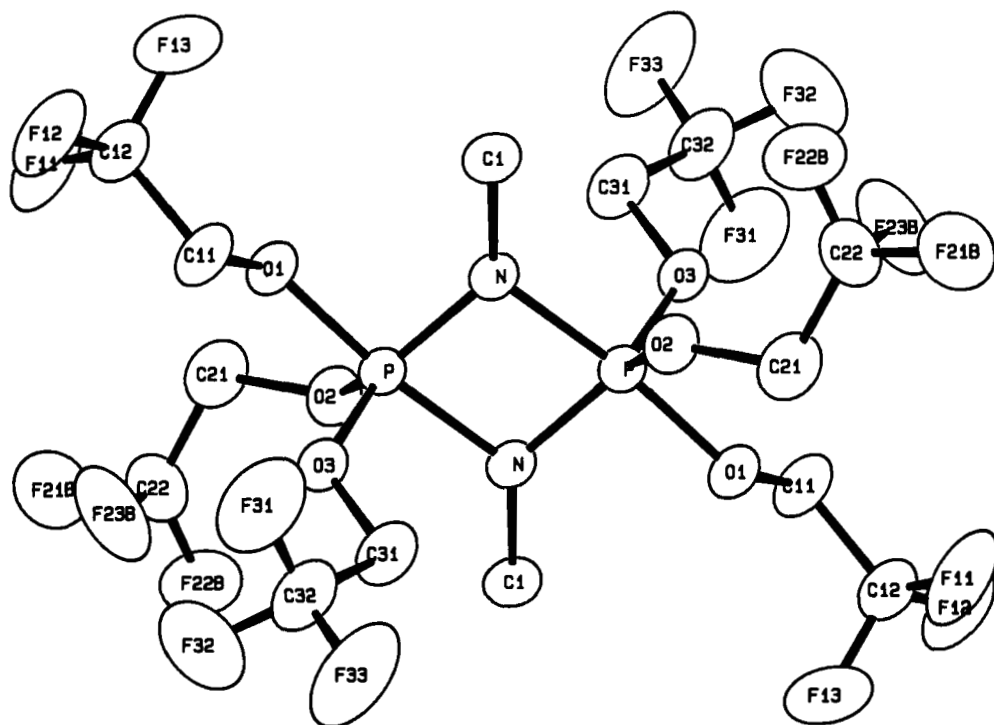


FIGURE 3 ORTEP plot of [MeNP(OCH$_2$CF$_3$)$_3$]$_2$, (2), with thermal ellipsoids at the 30% probability level. Atoms with the same label are related by a crystallographic inversion center (1−x, −y, 1−z). Hydrogen atoms are omitted for clarity. Only one set of positions for the disordered fluorine atoms bound to C22 is shown.

Atomic coordinates and selected bond lengths and angles are given in Tables I and II, respectively.

The two halves of the dimer are related by a crystallographic inversion center. The central $(PN)_2$ four-membered ring is therefore required by symmetry to be planar. Atoms C1 and O1 are displaced in opposite directions from this plane by distances of 0.247(5) Å and 0.125(3) Å, respectively. These displacements, and the enlarged angles of O1—P—N = 95.0(1)° and P—N—Cl = 130.3(2)° probably reflect a mitigation of crowding between the methyl group and the axial oxygen atom, where an H—O contact of 2.523 Å is observed (compared to the van der Waals' sum of 2.6 Å).

As a result of the displacement of C1 from the central plane, the geometry at the nitrogen atom is not precisely planar. The sum of the angles at nitrogen of 358.6(5) reflects this deviation from planarity.

The angles at phosphorus in the four-membered ring (79.0(1)°) are smaller than the angles at nitrogen (101.0(1)°). As a result the P—P distance across the ring (2.620(1) Å) is larger than the corresponding N—N distance (2.160(4) Å).

The geometry at the phosphorus atom is distorted trigonal bipyramidal. Distortions away from ideal trigonal bipyramidal geometry do not follow the Berry pseu-

TABLE I

Atomic Coordinates in Crystalline $[MeNP(OCH_2CF_3)_3]_2$[a]

| Atom[b] | x | y | z | B equiv[c] |
|---|---|---|---|---|
| P | 0.5021(1) | 0.1338(1) | 0.39493(9) | 3.61(2) |
| F11 | 0.4102(4) | 0.6266(3) | 0.2996(4) | 10.8(1) |
| F12 | 0.1448(3) | 0.6242(3) | 0.4094(3) | 9.59(9) |
| F13 | 0.2762(4) | 0.5387(3) | 0.5501(3) | 11.8(1) |
| F21A | 0.8754(8) | 0.4857(7) | −0.0863(6) | 9.3(2) |
| F21B | 0.9174(8) | 0.4619(7) | −0.1150(6) | 9.6(2) |
| F22A | 0.9967(8) | 0.251(1) | −0.0076(9) | 14.5(3) |
| F22B | 0.8968(8) | 0.2384(6) | −0.0543(6) | 9.8(2) |
| F23A | 0.7901(9) | 0.2634(8) | −0.0488(6) | 14.1(2) |
| F23B | 0.6612(7) | 0.3642(8) | −0.0019(6) | 10.6(2) |
| F31 | 0.0861(3) | 0.1681(4) | 0.3134(4) | 11.9(1) |
| F32 | 0.2835(4) | 0.1649(5) | 0.0878(3) | 13.9(1) |
| F33 | 0.1312(4) | −0.0333(4) | 0.2437(4) | 15.67(9) |
| 01 | 0.4390(3) | 0.3138(2) | 0.4013(2) | 4.27(6) |
| 02 | 0.6960(3) | 0.1855(3) | 0.2725(3) | 4.92(7) |
| 03 | 0.3968(3) | 0.1409(2) | 0.3010(2) | 4.64(6) |
| N | 0.4264(3) | 0.0596(3) | 0.5907(3) | 3.86(7) |
| C1 | 0.3012(5) | 0.1220(4) | 0.7227(4) | 5.2(1) |
| C11 | 0.2884(4) | 0.3892(4) | 0.4001(4) | 5.6(1) |
| C12 | 0.2808(5) | 0.5430(5) | 0.4131(5) | 6.2(1) |
| C21 | 0.7583(6) | 0.3342(5) | 0.1692(5) | 7.0(1) |
| C22 | 0.8331(7) | 0.3398(6) | 0.0033(5) | 8.3(2) |
| C31 | 0.3259(5) | 0.0134(5) | 0.3081(4) | 6.7(1) |
| C32 | 0.2067(5) | 0.0748(5) | 0.2399(5) | 8.7(1) |

[a] Numbers in parentheses are estimated standard deviations.
[b] Atoms are labeled to agree with Figure 3.
[c] Equivalent isotropic thermal parameters are calculated as $(4/3) [a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.

## TABLE II
Selected Distances (Å) and Angles (deg) for [MeNP(OCH₂CF₃)₃]₂[a]

| Atom 1 | Atom 2 | Distance | Atom 1 | Atom 2 | Distance |
|---|---|---|---|---|---|
| P | 01 | 1.666(2) | 01 | C11 | 1.407(4) |
| P | 02 | 1.604(2) | 02 | C21 | 1.417(4) |
| P | 03 | 1.611(3) | 03 | C31 | 1.412(6) |
| P | N | 1.630(2) | N | C1 | 1.461(4) |
| P | N' | 1.763(3) | | | |

| Atom 1 | Atom 2 | Atom 3 | Angle | Atom 1 | Atom 2 | Atom 3 | Angle |
|---|---|---|---|---|---|---|---|
| 01 | P | 02 | 91.3(1) | 03 | P | N' | 96.3(2) |
| 01 | P | 03 | 90.6(1) | N | P | N' | 79.0(1) |
| 01 | P | N | 95.0(1) | P | 01 | C11 | 126.4(3) |
| 01 | P | N' | 172.6(2) | P | 02 | C21 | 128.7(2) |
| 02 | P | 03 | 112.3(1) | P | 03 | C31 | 125.5(2) |
| 02 | P | N | 124.1(2) | P | N | P' | 101.0(1) |
| 02 | P | N' | 88.6(1) | P | N | C1 | 130.3(2) |
| 03 | P | N | 123.1(1) | P | N | C1' | 127.3(2) |

[a]Estimated standard deviations in parentheses. The atom labeling scheme is shown in Figure 3.

dorotation coordinate,[21] and most probably are a result of the constraint of the ring system and of mitigation of crowding in the molecule. The closing down of the equatorial angle O2—P—O3 to 112.3(1)° is accompanied by a nearly symmetrical opening up of the equatorial O—P—N angles (124.1(2)° and 123.1(1)°).

The sum of the equatorial angles at phosphorus is 359.5(4)° which indicates the near coplanarity of the four equatorial atoms (coplanar to within ±0.019 Å). The dihedral angle between the equatorial plane and the four-atom central plane is 85.2°. The largest of the axial-equatorial angles (O3—P—N' = 96.3(2)°) is accompanied by a short contact between hydrogen atoms on the neighboring atoms C31 and C1 (H312—H12 = 2.324 Å).

The axial P—O bond (1.666(2) Å) is somewhat longer than the equatorial P—O bonds (average 1.608(3) Å), as would be expected. The difference in length between the axial and equatorial P—N bonds is more pronounced (1.763(3) Å vs. 1.630(2) Å), where the equatorial bond is somewhat shorter than might be expected. Since the lone pair on the N atom is nearly in the equatorial plane of the P atom, backbonding might be invoked to explain the shortening of the P—N$_{eq}$ bond.

## EXPERIMENTAL

standard were assigned positive values. The IR spectra were recorded on a Carl-Zeiss UR-10 spectrometer either in Nujol mull or in KBr discs. The mass spectra were obtained from a VG-ZAB-2F spectrometer (EI conditions, 70 eV, 200 $\mu$; source temperature 200°C). Elemental analyses were performed at the City University, London through the kind offices of Dr. S. A. Matlin.

*Synthesis of [MeNP(OCH₂CF₃)₃]₂ (2).* Trifluoroethanol (6.0 g, 60 mmol) and sodium (1.4 g) were stirred in diethyl ether (100 mL) for 6 h at 25°C. The solution was cooled to $-78$°C and (MeNPCl₃)₂ (3.3 g, 10 mmol) was added. The mixture was stirred while the temperature increased slowly to ambient and filtered. Solvent was removed from the filtrate under reduced pressure to give the title compound (4.6 g, 64%) which was recrystallized from Et₂O, mp 80–82°C. IR (Nujol): 1420(m), 1370(m), 1290(s, br), 1225(m), 1190(s), 1180(s), 1175(s), 1160(s), 1135(s), 1105(s), 970(s), 890(s), 855(s), 840(s), 785(m), 765(s), 730(m), 695(m), 650(w), 620(w), 600(m), 585(m), 535(w) cm$^{-1}$. MS: m/z = 615 and 357 which correspond to (M—OCH₂CF₃)$^+$ and M$^+$/2 ions respectively. Analysis calculated for C₁₄H₁₈F₁₈N₂O₆P₂: C, 23.5; H, 2.5; N, 3.9. Found: C, 23.4; H, 2.5; N, 3.8. ¹H NMR: $\delta$ 2.44 (t, $J_{PH}$ = 13 Hz), $\delta$ 4.20 (dq with virtual coupling, $J_{PH}$ = 16 Hz, $J_{FH}$ = 8 Hz). ³¹P NMR (CHCl₃); $\delta$ $-71.8$(s). ¹⁹F NMR (C₆H₆): $\delta$ $-77.7$ (t, $J_{HF}$ = 8 Hz).

*Synthesis of [MeNP(OPh)₃]₂ (3).* The title compound was prepared by the treatment of (MeNPCl₃)₂ (1) (3.3 g, 10 mmol) with sodium phenoxide (7.0 g, 60 mmol) in diethyl ether. The product was purified by washing with methanol and extraction with chloroform (3 × 50 mL). The chloroform extract was evaporated to give 3 (4.0g, 59%), mp 140–150°C (decomp.) IR (Nujol): 1595(s), 1500(s), 1430(w), 1295(w), 1250(m), 1220(s), 1205(s), 1175(s), 1080(m), 1035(m), 1005(w), 940(s), 915(s), 910(s), 890(s), 865(s), 840(m), 770(s), 760(s), 740(s), 695(m), 680(w), 590(w), 520(m), 505(m) cm$^{-1}$. ¹H NMR: $\delta$ 2.53(t, $J_{PH}$ = 13 Hz), $\delta$ 6.89–7.26(m). ³¹P NMR: $\delta$ $-77.4$(s). The compound decomposes in solution.

*Synthesis of PhN=P(OCH₂CF₃)₃ (6).* Treatment of (PhNPCl₃)₂ (5) (4.57 g, 10 mmol) with sodium trifluoroethoxide (7.4 g, 60 mmol) in diethyl ether gave PhN=P(OCH₂CF₃)₃ (6) which was separated from the reaction mixture by distillation under vacuum, bp 66–68°C/0.2 torr, yield 2.2 g (26%). IR (Neat): 2975(w), 2900(w), 1600(m), 1500(m), 1440(w), 1420(m), 1385(m), 1305(s), 1285(s), 1255(s), 1235(s), 1175(s), 1100(s), 1075(m), 1040(m), 1010(m), 965(s), 890(m, br), 850(m, br), 760(w), 565(w), 535(w), 500(w) cm$^{-1}$. MS: m/z = 419 (100%) which corresponds to the M$^+$ ion. Analysis, calculated for C₁₂H₁₁F₉NO₃P: C, 34.4; H, 2.6; N, 3.3. Found: C, 32.8; H, 2.6; N, 3.0. ¹H NMR: $\delta$ 4.20 (dq, $J_{PH}$ = 8 Hz, $J_{FH}$ = 8 Hz); $\delta$ 6.70–7.30(m). ³¹P NMR: $\delta$ $-16.7$.

*Interconversion Among (Trifluoroethoxy and Fluoro Diazadiphosphetidines).* The compounds [(MeN)PF₃]₂ and [(MeN)P(OCH₂CF₃)₃]₂ (2) were mixed in the molar ratios of 1:2.7, 1:2.2, 1:1, 2:1 and 2.5:1 in CDCl₃ solvent contained in NMR tubes. The ¹H and ³¹P NMR spectra of the solutions were recorded at different intervals of time.

*X-Ray Crystal Structure Determination of [MeNP(OCH₂CF₃)₃]₂ (2).* The X-ray crystallographic study was done using an Enraf-Nonius CAD4 diffractometer and graphite monochromated molybdenum radiation ($\lambda K\bar{\alpha}$ = 0.71073 Å) at an ambient temperature of 23 $\pm$ 2°C. The colorless crystal used for the study (mounted in a thin-walled glass capillary tube which was sealed as a precaution against moisture sensitivity) was cut from a mass of chunky crystals and had dimensions of 0.30 x 0.33 x 0.35 mm.

*Crystal Data.* (C₇H₉O₃F₉PN)₂, triclinic space group P$\bar{1}$ [C$_i^1$ — No. 2],[10] a = 9.024(2) Å, b = 9.255(2) Å, c = 9.944(2) Å, $\alpha$ = 69.68(2)°, $\beta$ = 60.16(2)°, $\gamma$ = 78.88(2)°, Z = 1 and $\mu_{MoK\bar{\alpha}}$ = 3.37 cm$^{-1}$. A total of 1552 independent reflections ($+$h, $\pm$k, $\pm$l) was measured by use of the $\theta$-2$\theta$ scan mode with 3° $\leq$ 2$\theta_{MoK\bar{\alpha}}$ $\leq$ 43°. No corrections were made for absorption.

The structure was solved by use of direct methods and difference Fourier techniques and was refined by full-matrix least-squares.[11] One of the independent perfluoromethyl groups was found to be disordered, with two rotationally related sets of positions for the three fluorine atoms. These three atoms were refined anisotropically as six atoms in half occupancy. The remaining 18 independent nonhydrogen atoms were refined anisotropically. The 9 independent hydrogen atoms were included in the refinement as fixed isotropic scatteres (regularized difference Fourier positions for the methyl hydrogen atoms; ideal positions for the remainder). The final agreement factors[12] were R = 0.044 and R$_w$ = 0.061 for the 1301 reflections with I $\geq$ 3$\sigma_I$.

All computations were performed on a Microvax II computer using the Enraf-Nonius SDP system of programs.

## CONCLUSION

From the results of this study, stabilization of cyclodiphosphazanes in their dimeric forms (Scheme 1) is promoted by a sufficient combination of electron withdrawal at phosphorus and electron donation at the nitrogen center. The latter electronic requirements may favor more delocalized N—P—N bonding found in the dimeric system compared to the isolated P=N bonding present in the monomeric form. Thus, $[MeNP(OCH_2CF_3)_3]_2$ (2) has the dimeric formulation in contrast to the monomeric representation for the corresponding phenyl derivative (6). Likewise $[MeNP(OPh)_3]_2$ containing the more electronegative phenoxy group is dimeric, whereas $MeN=P(OMe)_3$ and $MeN=P(NMe_2)_3$ are monomeric.

## SUPPLEMENTARY MATERIAL AVAILABLE

Tables of thermal parameters, additional bond lengths and angles, and hydrogen atom parameters, Tables S1–S3, respectively (4 pages) have been deposited with the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW.

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11. The function minimized was $\Sigma w(|F_o| - |F_c|),^2$ where $w^{1/2} = 2FoLp/\sigma_1$.
12. $R = \Sigma| |F_o| - |F_c| |/\Sigma/|F_o|$ and $R_w = \{\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2\}^{1/2}$.
13. The $^{31}P$ chemical shifts for $(MeNPCl_3)_2$, $(MeNPF_3)_2$, and $(PhNPCl_3)_2$ are $-76.0$, $-70.3$, and $-77.0$ $\delta$ in $CHCl_3$.
14. A value of 1307 cm$^{-1}$ is reported for $v(P=N)$ in $MeN=P(OMe)_3^2$.
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