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FULL PAPER

Ring opening of bicyclic tertiary amines with cyclic chlorocarbaphosphazenes: reactions of $(ClCN)_2(Cl_2PN)$ with 1,4-diazabicyclo[2.2.2]octane and quinuclidine †

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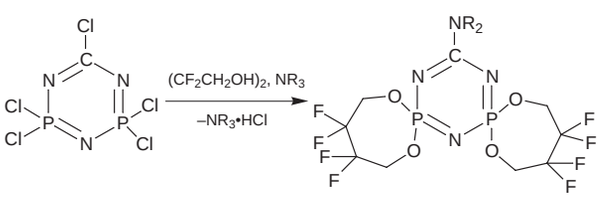
Reactions of bicyclic tertiary amines, 1,4-diazabicyclo[2.2.2]octane (DABCO) and quinuclidine, have been carried out with tetrachlorocyclodicarbaphosphatriazene, $(ClCN)_2(Cl_2PN)$, and with $(ClCN)_2(Cl_2PN)$ together with another acyclic tertiary amine. Reaction of an acyclic tertiary amine [NEt_3, $N(n\text{-}Pr)_3$, $NEt(i\text{-}Pr)_2$ or $Me_2NCH_2NMe_2$] with the chlorocarbaphosphazene followed by DABCO in 1 : 1 : 1 molar ratio proceeds with cleavage of a C–N bond of both tertiary amines. The cleaved alkyl group of DABCO remains as an alkyl chloride on the product molecule. The 4-(2-chloroethyl)piperazino derivatives of carbaphosphazenes, $(R_2NCN)[ClCH_2CH_2N(CH_2CH_2)_2NCN](Cl_2PN)$ [$R_2N = NEt_2$ **1**, $N(n\text{-}Pr)_2$ **2**, $NEt(i\text{-}Pr)$ **3** or NMe_2 **4**] were isolated, purified and characterized by spectral and analytical methods. Reaction of $(ClCN)_2(Cl_2PN)$ with two moles of DABCO gave the compound $[ClCH_2CH_2N(CH_2CH_2)_2NCN]_2(Cl_2PN)$ **5**. The 4-(2-chloroethyl)piperidino compound $[ClCH_2CH_2CH(CH_2CH_2)_2NCN]_2(Cl_2PN)$ **6** was obtained in the reaction of $(ClCN)_2(Cl_2PN)$ with two moles of quinuclidine, while $(Me_2NCN)[ClCH_2CH_2CH(CH_2CH_2)_2NCN](Cl_2PN)$ **7** is the product in its reaction with $Me_2NCH_2NMe_2$ and quinuclidine in 1 : 1 : 1 molar ratio. The crystal structure of compound **4** has been determined and shows differences in the exocyclic N–C bond distances of the piperazino group in its bonding to the 2-chloroethyl and carbaphosphazene moieties.

Introduction

The profound difference in structure, reactivity and stability of cyclocarbaphosphazenes in comparison to cyclophosphazenes has been reported by various groups. Roesky and Mainz[1] have shown from selected reactions the regiospecificity observed in substitution reactions on the carbon and phosphorus sites of chlorinated cyclocarbaphosphazenes. The differences in structure and thermal properties of substituted cyclocarbaphosphazenes in comparison to cyclophosphazenes as well as their use as additives in arresting the degradation of perfluorinated fluids have also been well documented.[2,3] Quite recently, Shreeve and co-workers[4] have reported that, unlike cyclophosphazenes, chlorinated cyclocarbaphosphazenes initiate C–N bond cleavage of trialkylamines with the regiospecific substitution of the dialkylamino group on the ring carbon atom of the carbaphosphazene. While amine hydrochloride is reported



as the only isolable side product from these reactions of carbaphosphazenes with trialkylamines,[4] the formation of tetraalkylammonium halide as well as alkyl halide has been envisaged for dealkylation reactions involving various amines and heteroaromatic halides.[5–9]

The present work has been designed so as to trap the cleaved alkyl group of tertiary amines as part of the product molecule in reactions involving cyclocarbaphosphazene and tertiary amines. Reports on dealkylations involving cyclic tertiary amines like *N*-methylmorpholine and *N*-methylpiperidine have shown the preference for the formation of products resulting from the cleavage of the methyl groups thereby indicating the extra stability of cyclic amines.[4] It is also therefore of prime interest to observe how aliphatic bicyclic tertiary amines and diamines will respond to a reaction with chlorocarbaphosphazene. By carrying out reactions of 1,4-diazabicyclo[2.2.2]-octane (DABCO) as well as quinuclidine with $(ClCN)_2(Cl_2PN)$ and with $(ClCN)_2(Cl_2PN)$ and another acyclic tertiary amine, we have been able to obtain stable soluble products wherein the ring opened bicyclic amine is found to substitute regiospecifically on the hybrid heterocycle. Details of these reactions as well as the crystal structure characterization of one of the ring-opened products are reported herein.

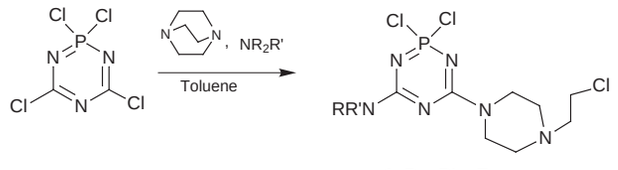
Results and discussion

Unlike simple trialkylamines, reactions of tertiary diamines such as DABCO, TMEDA and 1,4-dimethylpiperazine with chlorocarbaphosphazenes have been observed to result in the formation of large amounts of insoluble solids. For example, an equimolar reaction of DABCO and $(ClCN)_2(Cl_2PN)$ has been observed to give 75% w/w of a white solid which is insoluble in common organic solvents. However the reaction of $(ClCN)_2(Cl_2PN)$ with one mole of an acyclic tertiary amine followed by one mole of DABCO is found to result in the formation of soluble products wherein both the dealkylated acyclic amine and ring cleaved DABCO are found to substitute regiospecifically on the ring carbon atoms of the heterocycle (Scheme 1). The cleaved alkyl part of DABCO is found to remain as a CH_2CH_2Cl group on the piperazino ring.

Reaction of $(ClCN)_2(Cl_2PN)$ with DABCO in 1 : 2 molar ratio is found to yield, along with an insoluble white solid (40% w/w), a soluble product $[ClCH_2CH_2N(CH_2CH_2)_2NCN]_2(Cl_2PN)$ **5** where two ring opened DABCO units are substituted regiospecifically on the ring carbon atoms of the heterocycle (Scheme 2).

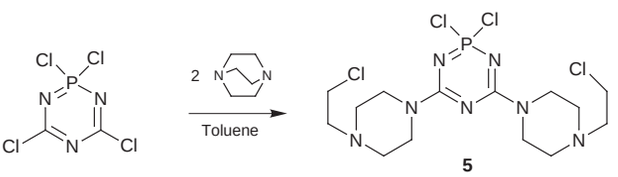
A similar reaction of the chlorocarbaphosphazene with quinuclidine in 1 : 2 molar ratio is found to result in 79% yield of

† Dedicated to Professor Jean'ne M. Shreeve on the occasion of her 65th birthday.



1 R = R' = Et
2 R = R' = n-Pr
3 R = i-Pr, R' = Et
4 R = R' = Me

Scheme 1



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Scheme 2

compound **6** where two ring cleaved quinuclidine moieties are substituted on the ring carbon atoms of carbaphosphazene. Unlike the reactions of DABCO, formation of insoluble products is not observed in this reaction. Compound **7**, which has one ring cleaved quinuclidine as well as one dimethylamino group substituted on the heterocycle, has also been prepared in a similar manner (Scheme 3).

6 NRR' = $ClCH_2CH_2[CH(CH_2CH_2)_2N]$
7 NRR' = NMe_2

Scheme 3

Compounds **1**–**7** are solids or viscous liquids and have been purified by column chromatography. As has been observed previously, the amine hydrochloride of the acyclic amine is also obtained as a side product in reactions where it has been used.[4] The yields of the purified products vary from 32 to 82% with the maximum for the reaction with NEt(*i*-Pr)$_2$. The formation of **3** indicates that sterically hindered trialkylamines, which are considered as non-nucleophiles, can also be made to undergo dealkylation with chlorocarbaphosphazenes. It is noteworthy that insoluble products are obtained only in the reactions of DABCO and not quinuclidine with the carbaphosphazene.

The structure of $(Me_2NCN)[ClCH_2CH_2N(CH_2CH_2)_2NCN](Cl_2PN)$ **4** is confirmed by a single crystal X-ray diffraction study (Fig. 1). The 4-(2-chloroethyl)piperazino group formed as a result of the ring cleavage of DABCO is substituted on one of the ring carbon atoms with the chloroethyl group oriented away from the carbaphosphazene ring. The exocyclic C–N bond distances of the piperazino ring to the carbaphosphazene and chloroethyl group are quite different. While C(1)–N(4), the bond between carbaphosphazene and piperazino group is 1.349 Å showing a distinct double bond character, C(9)–N(5), the bond between the latter and chloroethyl group, is 1.464 Å which is well within the range of the other C–N single bonds in the compound. Further the sum of the angles on N(4) is 358.5° indicating an sp^2 hybridization and the same on N(5) is 331.9° which is more pyramidal in nature. Selected bond distances and angles are given in Table 1. The ^{1}H NMR data on the NCH_2 groups of compounds **1**–**7** support this observation further. While the NCH_2 groups of DABCO are observed at δ 2.80, the carbaphosphazene bound NCH_2 groups of the 4-(2-chloroethyl)piperazino moiety of **1**–**5** are observed at δ 3.70–3.82 indicating significant deshielding. The 2-chloroethyl bound NCH_2 groups are observed at δ 2.46–2.52. Spectral data are similar for compounds **6** and **7** and quinuclidine has also been reported to undergo a similar ring opening on reaction with $CF_3ClC{=}SO$ as well as $CF_3C(O)Cl$.[10] The mass spectra of compounds **1**–**7** show the molecular ion peak with the expected peak pattern for the varying number of chlorines present. In addition to fragments due to the loss of chlorines, peaks assignable to the substituted imino moieties formed as a result of ring degradation of the piperazino and piperidino groups are also observed in all cases.

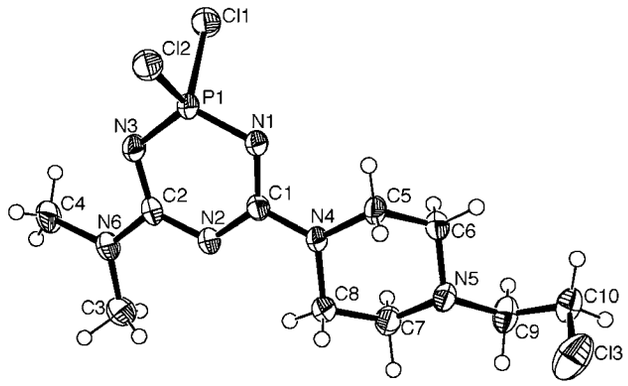

Fig. 1 Molecular structure of compound **4**.

Table 1 Selected bond distances (Å) and angles (°) for compound **4**

Cl(1)–P(1)	2.0175(7)	Cl(3)–C(10)	1.783(3)
Cl(2)–P(1)	2.0156(7)	N(4)–C(5)	1.463(2)
P(1)–N(1)	1.578(2)	N(4)–C(8)	1.466(3)
P(1)–N(3)	1.583(2)	N(5)–C(6)	1.457(3)
N(1)–C(1)	1.368(2)	N(5)–C(9)	1.464(3)
N(2)–C(2)	1.347(2)	N(5)–C(7)	1.467(3)
N(2)–C(1)	1.348(2)	N(6)–C(2)	1.349(2)
N(3)–C(2)	1.368(3)	N(6)–C(3)	1.461(3)
N(4)–C(1)	1.349(2)	N(6)–C(4)	1.467(3)
N(1)–P(1)–N(3)	116.61(9)	N(3)–P(1)–Cl(1)	110.48(7)
N(1)–P(1)–Cl(2)	110.02(7)	N(1)–P(1)–Cl(1)	109.35(7)
N(3)–P(1)–Cl(2)	110.03(7)	Cl(2)–P(1)–Cl(1)	98.91(3)
C(1)–N(1)–P(1)	114.38(13)	C(2)–N(2)–C(1)	119.5(2)
C(2)–N(3)–P(1)	113.76(13)	C(1)–N(4)–C(5)	122.0(2)
C(1)–N(4)–C(8)	122.2(2)	C(5)–N(4)–C(8)	114.2(2)
C(6)–N(5)–C(9)	112.6(2)	C(6)–N(5)–C(7)	108.5(2)
C(9)–N(5)–C(7)	111.1(2)	C(2)–N(6)–C(3)	121.2(2)
C(2)–N(6)–C(4)	120.5(2)	C(4)–N(6)–C(4)	118.1(2)
N(2)–C(1)–N(4)	116.9(2)	N(2)–C(1)–N(1)	127.5(2)
N(4)–C(1)–N(1)	115.6(2)		

Concluding remarks

The isolation and characterization of compounds **1**–**7** resulting from the ring opening reactions of DABCO and quinuclidine with $(ClCN)_2(Cl_2PN)$ shows that the cleaved alkyl group in dealkylation reactions of trialkylamines with chlorocarbaphosphazene remains initially as an alkyl chloride. The crystal structure of **4** provides the first structural evidence for this phenomenon. Since the mode of dealkylation of trialkylamines with $(ClCN)(Cl_2PN)_2$,[4] $(ClCN)_2(ClSN)$[9] and $(ClCN)_3$[5] has been found to proceed in a fashion similar to that of $(ClCN)_2(Cl_2PN)$, one can possibly assign a generality to this observation. The isolation of amine hydrochloride from reactions of trialkylamines with carbaphosphazenes[4] as well as the proposed formation of tetraalkylammonium chloride[8] can be envisaged as an outcome of further reaction of the cleaved alkyl halide as has been observed in the case of the von Braun cyanogen bromide reaction.[11] Dealkylation reactions of *N*-methylmorpholine and *N*-methylpiperidine with chlorocarbaphosphazenes did not show any evidence of ring cleaved products.[4] However the present study shows that bicyclic tertiary amines can be made to undergo ring cleavage with chlorocarbaphosphazenes and by careful control of the reaction parameters one can obtain stable ring cleaved products of the bicyclic amines.

Experimental

Materials

1,4-Diazabicyclo[2.2.2]octane, quinuclidine (Fluka), triethylamine, tri-*n*-propylamine and *N,N*-diisopropylethylamine (Lancaster) were dried and distilled prior to use. Tetrachlorocyclodicarbaphosphatriazene[12] and tetramethylmethylenediamine[13] were made by literature methods. Hexane, toluene, ethyl acetate and light petroleum (bp 60–80 °C) were dried and distilled by standard procedures.

General procedures

A conventional vacuum line equipped with dry nitrogen facility and Schlenk glassware was used for all reactions. Reactions were carried out and worked up under an atmosphere of dry nitrogen. Separation of solids from reaction mixtures was performed by slow filtration using a frit. Infrared spectra were recorded on a Perkin-Elmer 1320 spectrometer as Nujol mulls, ^{1}H, ^{13}C and ^{31}P NMR spectra using a Bruker WM-400 or a JEOL JNM-PMX60SI spectrometer with $CDCl_3$ as solvent and TMS and H_3PO_4 as references and mass spectra on a JEOL D-300 (EI/CI) spectrometer in the EI mode. Analyses were carried out on a Carlo Erba CHNS-O 1108 elemental analyzer.

Reactions of $(ClCN)_2(Cl_2PN)$

With triethylamine and DABCO in 1:1:1 ratio. Tetrachlorocyclodicarbaphosphatriazene (0.33 g, 1.38 mmol) was taken in a dry 50 cm^3 round bottom flask under nitrogen and toluene (15 cm^3) added. The mixture was stirred well and triethylamine (0.14 g, 1.38 mmol) added dropwise using a syringe. The flask was fitted with a condenser and kept in an oil-bath with the bath temperature increased to 110 °C. After 4 h of stirring a solution of DABCO (0.16 g, 1.43 mmol) in toluene (5 cm^3) was added over 5 min. The mixture was then stirred vigorously and maintained at this temperature for 24 h. The solution was brought to room temperature and filtered using a frit. The filtrate was evaporated and hexane (10 cm^3) added. The clear solution was decanted and the solvent evaporated to yield a solid. This was washed twice with cold hexane (2 cm^3), dried and identified as $(Et_2NCN)[ClCH_2CH_2N(CH_2CH_2)_2NCN](Cl_2PN)$ **1** (0.32 g, 60%) (Found: C, 37.25; H, 5.59; N, 21.83. $C_{12}H_{22}Cl_3N_6P$ requires C, 37.31; H, 5.70; N, 21.76%); $\tilde{\nu}_{max}$/cm^{-1} 1350s, 1300m, 1285w, 1260m, 1215w, 1070m, 1005m, 965w, 900m, 755w and 730w (Nujol); δ_H 1.10 (6 H, t, $2NCH_2CH_3$), 2.46 [4 H, t, $N(CH_2CH_2)_2N(CH_2)_2Cl$], 2.70 (2 H, t, NCH_2CH_2Cl), 3.28 (2 H, t, NCH_2CH_2Cl), 3.46 (4 H, q, $2NCH_2CH_3$) and 3.74 [4 H, t, $N(CH_2CH_2)_2N(CH_2)_2Cl$]; δ_C 12.96 (NCH_2CH_3), 36.92 (NCH_2CH_3), 41.82 [$N(CH_2CH_2)_2N(CH_2)_2Cl$], 43.73 [$N(CH_2CH_2)_2N(CH_2)_2Cl$], 50.29 (NCH_2CH_2Cl), 55.73 (NCH_2CH_2Cl), 154.38 [d, J(CP) 9.8, NCN] and 154.83 [d, J(CP) 7.6 Hz, NCN]; δ_P 57.30 (s); *m*/*z* 386 (M^+, 6), 350 ($M^+ - HCl$, 9), 268 ($Et_2NC_2N_3PCl_2NHCH_2$, 74), 240 ($Et_2NHC_2N_3PCl_2NHCH_2$, 14), 72 (Et_2N, 100) and 56 [$N(CH_2CH_2)_2$ NCH_2CH_2, 45%].

With tri-*n*-propylamine and DABCO in 1:1:1 ratio. The reaction of tetrachlorocyclodicarbaphosphatriazene (0.49 g, 2.05 mmol) with tripropylamine (0.30 g, 2.10 mmol) and DABCO (0.23 g, 2.05 mmol) was carried out and worked up as described for the synthesis of compound **1**. The viscous semisolid obtained was purified by column chromatography on silica gel using light petroleum–chloroform (1:1 v/v) to get needle like crystals of $(n\text{-}Pr_2NCN)[ClCH_2CH_2N(CH_2CH_2)_2NCN](Cl_2PN)$ **2** (0.23 g, 32%), mp 73–75 °C (Found: C, 40.46; H, 6.37; N, 20.40. $C_{14}H_{26}Cl_3N_6P$ requires C, 40.58; H, 6.28; N, 20.29%); $\tilde{\nu}_{max}$/cm^{-1} 1350s, 1305m, 1290m, 1255s, 1205w, 1130w, 1095m, 1075m, 1035m, 1000m, 980m, 870w, 750m and 730s (Nujol); δ_H 0.90 (6 H, t, $2NCH_2CH_2CH_3$), 1.60 (4 H, m, $2NCH_2CH_2CH_3$), 2.50 [4 H, t, $N(CH_2CH_2)_2NCH_2CH_2Cl$], 2.78 [2 H, t, $N(CH_2CH_2)_2NCH_2CH_2Cl$], 3.40 (4 H, t, $2NCH_2CH_2CH_3$), 3.60 (2 H, t, NCH_2CH_2Cl) and 3.80 [4 H, t, $N(CH_2CH_2)_2NCH_2CH_2Cl$]; δ_C 11.45 (d, $NCH_2CH_2CH_3$), 21.24 (d, $NCH_2CH_2CH_3$), 40.34 [$N(CH_2CH_2)_2N(CH_2)_2Cl$], 42.74 [$N(CH_2CH_2)_2N(CH_2)_2Cl$], 48.93, 49.42 ($NCH_2CH_2CH_3$), 52.87 (NCH_2CH_2Cl), 59.58 (NCH_2CH_2Cl), 163.30 [d, J(C–P) 9.5, NCN] and 163.80 [d, J(C–P) 7.6 Hz, NCN]; δ_P 57.25 (s); *m*/*z* 378 ($M^+ - HCl$, 5), 379 ($M^+ - Cl$, 6), 295 ($Pr_2NC_2N_3PCl_2NCH_2$, 100), 100 (Pr_2N, 20) and 182 ($Cl_2NPN_3C_2NH$, 20%).

With *N,N*-diisopropylethylamine and DABCO in 1:5:1 ratio. To a solution of tetrachlorocyclodicarbaphosphatriazene (0.49 g, 2.05 mmol) in toluene (10 cm^3) *N,N*-diisopropylethylamine (1.33 g, 10.29 mmol) was added dropwise. After stirring the mixture for 10 h at 110 °C a solution of DABCO (0.23 g, 2.05 mmol) in toluene (5 cm^3) was added over 5 min. The mixture was then stirred for 24 h at 120 °C, cooled to room temperature and filtered using a frit. The filtrate was evaporated to dryness, 10 cm^3 of hexane added and the clear solution was decanted. The viscous liquid obtained on evaporation of this solution was purified by column chromatography under a nitrogen atmosphere on silica gel using light petroleum–chloroform (1:1 v/v) as eluent. The purified product was a viscous liquid characterized as $[(Et)(i\text{-}Pr)NCN][ClCH_2CH_2N(CH_2CH_2)_2NCN](Cl_2PN)$ **3** (0.68 g, 82%) (Found: C, 38.67; H, 5.68; N, 21.00. $C_{13}H_{23}Cl_3N_6P$ requires C, 38.85; H, 5.72; N, 20.92%); $\tilde{\nu}_{max}$/cm^{-1} 1350s, 1340s, 1310m, 1290w, 1260s, 1210m, 1190vw, 1130m, 1100w, 1075m, 1040m, 1000s, 950w, 900s and 860w (Nujol); δ_H 1.10 [9 H, m, $CH_3CH_2NCH(CH_3)_2$], 2.48 [4 H, t, $N(CH_2CH_2)_2NCH_2CH_2Cl$], 2.70 [2 H, t, $N(CH_2CH_2)_2NCH_2CH_2Cl$], 3.35 (2 H, q, NCH_2CH_3), 3.54 (2 H, t, NCH_2CH_2Cl), 3.70 [4 H, t, $N(CH_2CH_2)_2NCH_2CH_2Cl$] and 4.82 [1 H, m, $NCH(CH_3)_2$]; δ_P 56.96 (s); *m*/*z* 371 ($M^+ - C_2H_5$, 32), 336 ($M^+ - C_2H_5Cl$, 13), 301 ($M^+ - C_2H_5Cl_2$, 9), 288 [$M^+ - (C_2H_4Cl + CH_2Cl)$, 100], 245 ($MeNC_2N_3PClNC_4H_8N$, 11) and 216 ($NC_2N_3PClNC_4H_8N$, 9%).

With tetramethylmethylenediamine and DABCO in 1:1:1 molar ratio. To a solution of tetrachlorocyclodicarbaphosphatriazene (1.25 g, 5.23 mmol) in toluene (15 cm^3) at 0 °C tetramethylmethylenediamine (0.53 g, 5.20 mmol) was added dropwise. After stirring the mixture at 60 °C for 6 h, a solution of DABCO (0.59 g, 5.27 mmol) in toluene (5 cm^3) was added over 5 min. The mixture was then stirred for 24 h at 120 °C and cooled to room temperature. The clear solution was decanted and evaporated to dryness. The residue was extracted with warm hexane (5 cm^3), decanted and kept at 0° C for 24 h to get colorless crystals of $(Me_2NCN)[ClCH_2CH_2N(CH_2CH_2)_2NCN](Cl_2PN)$ **4** (1.37 g, 73%), mp 80–82 °C (Found: C, 33.10; H, 4.95: N, 23.30. $C_{10}H_{18}Cl_3N_6P$ requires C, 33.37; H, 5.01; N, 23.36%); $\tilde{\nu}_{max}$/cm^{-1} 1550m, 1400s, 1350s, 1340s, 1300m, 1250m, 1150w, 1130w, 1070w, 990m, 980m, 840w and 810w (Nujol); δ_H 2.52 [4 H, t, $N(CH_2CH_2)_2N(CH_2)_2Cl$], 2.78 (2 H, t, NCH_2CH_2Cl), 3.10 (6 H, s, $2NCH_3$), 3.64 [2 H, t, $N(CH_2CH_2)_2NCH_2CH_2Cl$] and 3.82 [4 H, t, $N(CH_2CH_2)_2NCH_2CH_2Cl$]; δ_C 36.37, 36.47 (NCH_3), 40.68 [$N(CH_2CH_2)_2N(CH_2)_2Cl$], 42.92, 43.26 [$N(CH_2CH_2)_2N(CH_2)_2Cl$], 52.80 (NCH_2CH_2Cl), 59.60 (NCH_2CH_2Cl), 163.00 [d, J(C–P) 9.6, NCN] and 164.25 [d, J(C–P) 7.6 Hz, NCN]; δ_P 57.51 (s); *m*/*z* 358 (M^+, 1), 322 ($M^+ - HCl$, 6), 307 [$M^+ - (HCl + Me)$, 3], 287 [$M^+ - (HCl + Cl)$, 9], 279 [$M^+ - (NMe_2 + Cl)$, 8] and 240 ($Me_2NC_2N_3PCl_2NHCH_2$, 100%).

With DABCO in 1:2 ratio. Tetrachlorocyclodicarbaphosphatriazene (0.46 g, 1.93 mmol) in toluene (15 cm^3) was treated with a solution of DABCO (0.43 g, 3.84 mmol) in toluene (5 cm^3). Formation of a significant amount of a white solid was observed which remained even after stirring this mixture at 110 °C for 24 h. The insolubles were filtered off and the filtrate was evaporated to dryness to obtain a white solid of $[ClCH_2CH_2N(CH_2CH_2)_2NCN]_2(Cl_2PN)$ **5** (0.50 g, 56%), mp 125 °C

(Found: C, 35.62; H, 5.25; N, 21.10. $C_{14}H_{24}Cl_4N_7P$ requires C, 36.27; H, 5.18; N, 21.16%); δ_H 2.44 [8 H, t, $2NCN(CH_2CH_2)_2N$], 2.70 (4 H, t, $2NCH_2CH_2Cl$), 3.55 (4 H, t, $2NCH_2CH_2Cl$) and 3.78 [8 H, t, $2NCN(CH_2CH_2)_2N$]; δ_C 39.15 [$N(CH_2CH_2)_2N(CH_2)_2Cl$], 41.61, 41.98 [$N(CH_2CH_2)_2N(CH_2)_2Cl$], 51.79 (NCH_2CH_2Cl), 58.29 (NCH_2CH_2Cl) and 162.55 [d, J(C–P) 7.6 Hz, NCN]; δ_P 57.91 (s); m/z 461 (M^+, 7.0), 426 ($M^+ - Cl$, 30), 342 [$Cl(CH_2)_2N(CH_2CH_2)_2N(CN)_2NCH_2(NPCl_2)$, 57] and 237 [$(CH_2)_2N(CN)_2NCH_2(NPCl_2)$, 14%].

With quinuclidine in 1:2 ratio. To a solution of $(ClCN)_2(Cl_2PN)$ (0.63 g, 2.64 mmol) in toluene (15 cm^3) was added slowly a solution of quinuclidine (0.59 g, 5.30 mmol) in toluene (5 cm^3) with stirring. The mixture was refluxed for 24 h and filtered. The filtrate was evaporated to dryness and warm hexane (20 cm^3) added. The mixture was shaken well and the clear solution separated while warm. Reducing the volume to 5 cm^3 and storage at 0 °C overnight gave an amorphous white solid. This was further purified by chromatography on a silica gel column using light petroleum–chloroform (30:70 v/v) to yield a microcrystalline solid, $[ClCH_2CH_2CH(CH_2CH_2)_2NCN]_2(Cl_2PN)$ **6** (0.96 g, 79%), mp 115–118 °C (Found: C, 41.59; H, 5.70; N, 15.12. $C_{16}H_{26}Cl_4N_5P$ requires C, 41.65; H, 5.64; N, 15.18%); $\tilde{\nu}_{max}/cm^{-1}$ 1365s, 1350s, 1310m, 1290m, 1250s, 1230s, 1210w, 1150w, 1160w, 1135w, 1110w, 1070s, 1030m, 950w, 920w, 890w, 850w, 800w (br), 750w and 720m (Nujol); δ_H 1.19 (4 H, s, br, $2CH_2CH_2Cl$), 1.75 [10 H, t, $2\ N(CH_2CH_2)_2CH$], 2.81 (4 H, s, br), 3.59 (4 H, t) and 4.69 (4 H, s, br); δ_C 31.45 [$N(CH_2CH_2)_2CH$], 33.22 [$N(CH_2CH_2)_2CH$], 38.75 (CH_2CH_2Cl), 42.29 (CH_2CH_2Cl), 44.69, 43.91 [$N(CH_2CH_2)_2CH$] and 161.70 [d, J(C–P) 7.6 Hz, NCN]; δ_P 56.66 (s); m/z 459 (M^+, 24), 424 ($M^+ - Cl$, 29), 395 ($M^+ - C_2H_5Cl$, 18), 342 [$M^+ - CH_2CHCH(CH_2)(CH_2)_2Cl$, 11], 278 [$M^+ - CH_2CHCH(CH_2)(CH_2)_2Cl + C_2H_5Cl$, 12] and 145 [$N(CH_2CH_2)_2CCH_2CH_2Cl$, 100%].

With $Me_2NCH_2NMe_2$ and quinuclidine in 1:1:1 molar ratio. To a solution of $(ClCN)_2(Cl_2PN)$ (1.00 g, 4.19 mmol) in toluene (15 cm^3) was added slowly $Me_2NCH_2NMe_2$ (0.43 g, 4.22 mmol) and the mixture refluxed for 4 h. Afterwards the solution was brought to room temperature and quinuclidine (0.47 g, 4.23 mmol) in toluene (5 cm^3) added. The solution was further refluxed for 20 h and worked up as described for compound **6**. The white solid product was characterized as $(Me_2NCN)[ClCH_2CH_2CH(CH_2CH_2)_2NCN](Cl_2PN)$ **7** (1.00 g, 67%), mp 75–78 °C (Found: C, 36.92; H, 5.22; N, 19.20. $C_{11}H_{19}Cl_3N_5P$ requires C, 36.82; H, 5.30; N, 19.53%); $\tilde{\nu}_{max}/cm^{-1}$ 1370s, 1350s, 1290s, 1265s, 1235s, 1170w, 1120w, 1060s, 1020m, 990m, 980m, 970m, 960s, 910s, 860w, 800w, 750s, 720m and 630s (Nujol); δ_H 1.19 (2 H, s, br, CH_2CH_2Cl), 1.76 [5 H, m, $N(CH_2CH_2)_2CH$], 2.82 (2 H, s, br), 3.11 (6 H, s, NMe_2), 3.58 (2H, t) and 4.69 (2 H, s, br); δ_C 31.47 [$N(CH_2CH_2)_2CH$], 33.29 [$N(CH_2CH_2)_2CH$], 36.53, 36.90 (NCH_3), 38.81 (CH_2CH_2Cl), 42.30 (CH_2CH_2Cl), 43.66, 44.16 [$N(CH_2CH_2)_2CH$], 161.68 [d, J(C–P) 9.6 Hz, NCN] and 162.70 [d, J(C–P) 7.6, NCN]; δ_P 56.76 (s); m/z 357 (M^+, 44), 322 ($M^+ - Cl$, 46), 294 [$M^+ - (CH_2)_2Cl$, 24], 286 [$M^+ - (HCl + Cl)$, 20], 240 [$M^+ - CH_2CHCH(CH_2)(CH_2)_2Cl$, 28], 211 [$M^+ - N(CH_2CH_2)_2CH(CH_2)_2Cl$, 30], 177 ($Me_2HNCNCNPClN$, 35) and 146 [$N(CH_2CH_2)_2CH(CH_2)_2Cl$, 100%].

Crystallography

Single crystals of $(Me_2NCN)[ClCH_2CH_2N(CH_2CH_2)_2NCN](Cl_2PN)$ **4** suitable for X-ray studies were obtained by slow crystallization under nitrogen from hexane at 0 °C.

Crystal data. $C_{10}H_{18}Cl_3N_6P$, $M = 359.62$, monoclinic, space group $P2_1/c$, $a = 9.4314(3)$, $b = 11.7824(3)$, $c = 14.6793(4)$ Å, $\beta = 91.9310(10)°$, $U = 1630.30(8)$ Å^3, $T = 213(2)$ K, $Z = 4$, μ(Mo-K$_\alpha$) = 0.659 mm^{-1}, 10 014 reflections measured, 3862 unique ($R_{int} = 0.0375$) which were used in all calculations. The final R indices [$I > 2\sigma(I)$] were $wR(F^2) = 0.0938$, $R1 = 0.0391$.

Structure solution and refinement. A Siemens SMART diffractometer with a CCD detector at −54 °C was employed, θ range for data collection 2.16 to 28.24°, limiting indices $-12 \leqslant h \leqslant 12$, $-15 \leqslant k \leqslant 15$, $-13 \leqslant l \leqslant 19$. The frame data were acquired using Siemens SMART software and processed on a SGI-Indy/Indigo 2 workstation by using the SAINT software.[14] The structure was solved by direct methods using the SHELX 90[15] program and refined by full matrix least squares on F^2 using SHELXL 93, incorporated in SHELXTL-PC V 5.03.[16] All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were located from the difference electron-density maps and included in the refinement process in an isotropic manner. A SADABS[17] absorption correction was made, maximum and minimum transmission 0.948857 and 0.719603.

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See http://www.rsc.org/suppdata/dt/1999/1515/ for crystallographic files in .cif format.

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