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Structural Investigations of Phosphorus-Nitrogen Compounds

7. Relationships between Physical Properties, Electron Densities, Reaction Mechanisms and Hydrogen-Bonding Motifs of $N_3P_3Cl_{(6-n)}(NHBu^t)_n$ Derivatives.

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Synopsis The crystal structures of $N_3P_3Cl_5(NHBu^t)$ and $N_3P_3Cl_2(NHBu^t)_4$ have been determined at 120K and those of $N_3P_3Cl_6$ and $N_3P_3Cl_4(NHBu^t)_2$ have been re-determined at 120K. These are compared with the known structure of $N_3P_3(NHBu^t)_6$, which was studied at 150K. Molecular parameters and hydrogen-bonding motifs are discussed and compared in the light of their physical and chemical properties.

Abstract. A series of compounds of the $N_3P_3Cl_{(6-n)}(NHBu^t)_n$ family (where $n = 0, 1, 2, 4$ and 6) are presented and their molecular parameters are related to trends in physical properties, which provides insight into a potential reaction mechanism for nucleophilic substitution. The crystal structures of $N_3P_3Cl_5(NHBu^t)$ and $N_3P_3Cl_2(NHBu^t)_4$ have been determined at 120K and those of $N_3P_3Cl_6$ and $N_3P_3Cl_4(NHBu^t)_2$ have been re-determined at 120K. These are compared with the known structure of $N_3P_3(NHBu^t)_6$ studied at 150K. Trends in molecular parameters (phosphazene ring, P-Cl & P-N($NHBu^t$) distances, PCl_2 angles and endo- and exocyclic phosphazene ring parameters) across the series are observed. Hydrogen-bonding motifs are identified, characterised and compared. Both the molecular and hydrogen bonding parameters are related to the electron distribution in bonds and the derived basicities of the cyclophosphazene series of compounds. These findings provide evidence for a proposed mechanism for nucleophilic substitution at a phosphorus site bearing a $PCl(NHBu^t)$ moiety.

Keywords: Structure-property relationships, cyclophosphazenes, hydrogen bonding, structural systematics

1. Introduction

During extensive investigations of the replacement patterns of chloride substituents in $N_3P_3Cl_6$ by amines (Shaw, 1976; Krishnamurthy et al 1976) the following conclusions were made:

- Primary amines, H_2NR , show a greater degree of variation in substitution patterns compared to secondary amines, HNR_2 .
- Most secondary amines follow a predominantly non-geminal path, in which a PCl_2 group is attacked in preference to a $PCl(NR_2)$ moiety.
- At di-substitution, $N_3P_3Cl_4(NHR)_2$, both geminal and non-geminal replacements occur, depending on the R group. For R = Et only non-geminal cis- and trans-derivatives were observed, for R = Prⁱ all three isomers, geminal and non-geminal, were obtained, whilst for R = Bu^t only the geminal derivative was isolated. Thus under comparable conditions, the increasing steric bulk of the group R causes a change from non-geminal to geminal substitution.
- At tetra-substitution, $N_3P_3Cl_2(NHR)_4$, a geminal pattern prevails.

Thus, when a cyclotriphosphazene compound containing PCl_2 groups is allowed to react with tertiary butylamine, H_2NBu^t , geminal $P(NHBU^t)_2$ moieties are formed with very few exceptions (Das et al, 1965; Begley et al, 1979; Krishnamurthy et al 1980, Coles et al, 2001), and so tertiary butylamine is the preferred reagent to introduce geminal $P(NHR)_2$ groupings into a cyclotriphosphazene derivative. The different substitution patterns have been explained by nucleophilic attack at different reaction sites, *viz.* at phosphorus or at the hydrogen atom of the $PCl(NHR)$ grouping giving rise to a proton abstraction/chloride ion elimination mechanism, which has been discussed elsewhere (Das et al, 1965; Ganapathiappan et al, 1987). If the phosphorus atom becomes more susceptible to nucleophilic attack, which occurs in $N_4P_4Cl_8$ (Krishnamurthy et al 1977 & 1978), the balance is tipped towards non-geminal replacements giving rise to $PCl(NHBU^t)$ moieties. H_2NBu^t is the most sterically hindered of the primary amines discussed, which is also borne out that under many reaction conditions only tetra-substitution, $N_3P_3Cl_2(NHBU^t)_4$, is usually achieved (Das et al, 1965), although the fully substituted derivative, $N_3P_3(NHBU^t)_6$, can be obtained under very drastic conditions (Das et al, 1965; Bickley et al, 2003). Whilst many other phosphazene derivatives containing P-Cl and P-NHR groupings are rather unstable, this does not seem to apply to tertiary butylamino-derivatives. In the present work the crystal structures of a series of tertiary butylamino-derivatives of cyclophosphazene have been determined and their molecular parameters and hydrogen-bonding motifs are discussed in the light of the physical and chemical properties of the compounds.

2. Experimental

2.1. Preparation of compounds

Hexachlorocyclotriphosphazene (**1**) (15g, 43.16 mmol) and tert-butylamine (12.6 g, 173 mmol) were dissolved in 200 mL dichloromethane under argon pressure in a 250 mL three-

necked round bottomed flask. The reaction mixture was stirred and refluxed in an oil-bath for 6 days. Tert-butylamine hydrochloride was filtered off and the solvent removed at 30°C. Two compounds were detected by TLC [$R_f = 0.6$ (**2**) and 0.3 (**3**), $N_3P_3Cl_4(NHBU^t)_2$,] using dichloromethane-*n*-hexane (1:2) as the mobile phase. The crude product was subjected to column chromatography on silica gel using dichloromethane/*n*-hexane (1:2) as eluent. 1-Tert-butylamino-1,3,3,5,5-pentachlorocyclotriphosphazene, (**2**), was separated and re-crystallised from *n*-hexane. Found: C 12.56%; H, 2.74%; N,14.66 % ; $(M+H)^+$, 384 $C_4H_{10}Cl_5N_4P_3$; Requires : C 12.50 % ; H, 2.62 % ; N, 14.58 % ; M 383.34. [m.p: 46°C (lit. -10 to -11°C, (Das, Keat, Shaw & Smith, 1965); 110°C, (Begley, Sowerby & Bamgboye, 1979)], 2g, yield 21 %) and 1,1-bis(tert-butylamino)-3,3,5,5-tetrachlorocyclotriphosphazene, (**3**), was separated and recrystallise from *n*-hexane–dichloromethane (1:1), Found : C 22.74 %; H, 4.68 %; N,16.15 % ; $(M+H)^+$, 421 $C_8H_{20}Cl_4N_5P_3$; Requires : C 22.82 % ; H, 4.79 % ; N, 16.63 % ; M ,421 [m.p: 120-122°C, lit. 120-122°C, (Das, Keat, Shaw & Smith, 1965); 121°C, (Begley, Sowerby & Bamgboye, 1979)], 4.35g, yield 24 %.

Details of the preparation of $N_3P_3Cl_2(NHBU^t)_4$ (**4**) have been reported elsewhere (Das, Keat, Shaw & Smith, 1965), with m.p. = 156°C from light petroleum.

2.2. X-ray crystallography

Data were collected at low temperature on an Nonius KappaCCD area detector diffractometer located at the window of a Nonius FR591 rotating anode X-ray generator, equipped with a molybdenum target ($\lambda_{Mo-K\alpha} = 0.71073\text{\AA}$). Structures were solved and refined using the SHELX-97 (Sheldrick, 1997) suite of programs. Data were corrected for absorption effects by means of comparison of equivalent reflections using the program SORTAV (Blessing, 1997). Non-hydrogen atoms were refined anisotropically, whilst hydrogen atoms were located from a difference map where the data quality allowed and freely refined isotropically (otherwise they were located in idealised positions with their thermal parameters riding on the values of their parent atoms). Although compound (**3**) crystallised in a chiral space group, the data were not of sufficient quality to refine the Flack parameter and hence determine the correct absolute structure. Pertinent data collection and refinement parameters are collated in Table 1.

Table 1

3. Discussion

3.1. Molecular structures

Changes in molecular parameters of cyclophosphazene derivatives have been investigated as a function of substituents at fixed positions (Coles et al, 2004a); the overall architecture of

these molecules remained the same and so the designation of bond length and bond angle parameters was unambiguous for such a series of compounds. The molecules in the present study have different degrees of substitution of Cl atoms by NHBu^t residues and this requires some modifications in the designation of their molecular parameters as summarised in figure 1. The endocyclic bond angle α is defined by N-P(X)₂-N, N-P(Y)₂-N, or N-P(XY)-N (X = Cl, Y = NHBu^t), the endocyclic bond angle β as (Y)₂P-N-P(X)₂ or (XY)P-N-P(X)₂, the endocyclic bond angle γ as N-P(X)₂-N and the endocyclic bond angle δ at (X)₂P-N-P(X)₂ or (Y)₂P-N-P(Y)₂. Analogous descriptions apply to definitions of the endocyclic bond lengths a , b , c , etc. as summarised in Figure 1. Selected molecular parameters for all the crystal structures used in this comparison are given in Table 2.

Fig. 1 and Table 2

Although the room temperature molecular structure of N₃P₃Cl₆, (**1**), has been reported (Bullen, 1971), a low temperature structure (depicted in figure 2) was determined for the purposes of accurate comparison in this study.

The structure of the two chemically-equivalent molecules in the asymmetric unit of N₃P₃Cl₅(NHBu^t), (**2**) is represented in figure 3 and a number of structural changes from (**1**) are observed. There is a significant decrease in α , with a corresponding increase in β , and smaller changes are observed in γ and δ (Table 2). There is a marked increase in bond length a and a marked decrease in b , whereas c is largely unaffected. The non-geminal P-Cl bond, d' , is longer than the corresponding bond lengths, d , of the PCl₂ group. The opposite behaviour is observed for the exocyclic P-N bond length e' , which is substantially shorter than those in geminal groups, e . Both effects have been observed in similar structures (Ahmed & Pollard, 1972b; Ahmed & Gabe, 1975; Ahmed & Fortier, 1980; Alkubaisi, Hursthouse, Shaw & Shaw, 1988; Beşli et al, 2002a; Beşli et al, 2002b; Coles et al, 2004b; Beşli et al, 2004a; Beşli et al, 2004b). The sum of the bond angles around the exocyclic N atom at 358.3° shows that it has trigonal planar character.

Fig. 2, 3

Although the crystal structure of N₃P₃Cl₄(NHBu^t)₂, (**3**), has been previously determined (Begley et al, 1979), the study was performed at room temperature and the data were of insufficient quality to determine hydrogen atom positions. As compound (**3**) is a typical example of a geminally di-substituted derivative of the type, N₃P₃Cl₄R₂, where R is a strongly electron-releasing substituent, an accurate structure (shown in figure 4) was determined at low temperature, so that the molecular parameters could be included in this work. The structure exhibits two chemically-equivalent molecules in the asymmetric unit. The bond lengths a at 1.619Å are relatively long, whereas those for b at 1.556Å are relatively short, giving a Δ (P-N) (= $a - b$) value of 0.063Å, one of the largest ones observed from a survey of the CSD (Allen,

2002). Concomitantly there is a very small bond angle α of 112.3° and a very large β angle of 123.5°. The exocyclic P-N bond length, e , of 1.616Å is quite short for this type of bond indicating extensive back-donation of the lone-pair of electrons on the N atom towards the P atom. This bond shortening might have been even shorter were it not for the conformation of the NHBu^t substituents, one of which is in almost complete Type II conformation, the other in between Type I and III (an explanation of these conformational types is given in Fincham et al, 1986). The back-donation is also demonstrated by the sum of the bond angles around the exocyclic N atoms of 358.8° showing their trigonal planar character. Increases in P-Cl bond lengths, d , and a decrease in bond angle Cl-P-Cl, ω , are also noted.

The crystal structure of N₃P₃Cl₂(NHBu^t)₄, (**4**), is presented in Figure 5. The effect on molecular parameters resulting from the large electron-releasing capacity of the NHBu^t substituents is also demonstrated in this compound, as the changes in some parameters are further enhanced compared to the di-substituted compound (**3**). The bond angle α of 114.4° bears this out, as do the respective bond lengths a and b of 1.623Å, 1.560Å giving a Δ (P-N)-value of 0.063Å. The averaged sum of bond angles around the exocyclic N atoms of 353.7° is the lowest in this series of compounds and indicates the greatest deviation from a trigonal planar structure.

Fig. 4, 5

The low temperature structure of N₃P₃(NHBu^t)₆, (**5**) has been reported previously (Bickley et al, 2003) with the CSD reference code GUZVIG, which is used for comparison in this study. As expected for such a symmetrically-substituted derivative, there are no statistically significant variations in the endocyclic P-N bond-lengths. The averaged sum of the bond angles around the exocyclic N atoms at 355.1° is also somewhat lower than those for compounds (**2**) and (**3**).

A measure of the conformational orientation of the NHBu^t groups relative to each other is given by the torsional angle to both adjacent ring N atoms and a measure of the close-packed nature of the NHBu^t groups is given by the non-bonded separation of the central carbon atoms between adjacent moieties (Table 3). It can be seen from Table 3 that there is a general decrease in this C...C distance for a corresponding increase in the number of NHBu^t groups situated about the N₃P₃ core. This trend is indicative of the fact that these groups are more tightly clustered around the core and hence impede any interactions with it, due to an increase in steric hindrance. Another indication of the close-packed nature of the NHBu^t groups is the torsion angle between the plane of the N₃P₃ ring and the rotation angle about the P-N bond (Table 3). With an increasing number of NHBu^t groups there is, on average, a corresponding increase in the torsion angle indicating that this group must increasingly twist away from its sterically unhindered optimal position (Type I conformation, Fincham et al, 1086).

Table 3

3.2. Hydrogen bonding

Hydrogen bonding in the crystal structure of **(2)**, $\text{N}_3\text{P}_3\text{Cl}_5(\text{NHBU}^t)$, is depicted in figure 6 and shows the formation of discrete head-to-tail dimers, containing an 8-membered ring as a result of donation from the $\text{BU}^t\text{N-H}$ moiety to the ring N atom of another molecule. The conformation of this ring is approximately saddle-shaped, with slightly different distances between donor and acceptor atoms of 3.079 Å and 3.095 Å, respectively.

The hydrogen bonding in the crystal structure of **(3)**, $\text{N}_3\text{P}_3\text{Cl}_4(\text{NHBU}^t)_2$, is presented in figure 7 and shows a similar structural arrangement to **(2)**, in which intermolecular hydrogen-bonds form an 8-membered ring of complementary dimers. The corresponding donor-acceptor separation distances of **(3)** are 3.123 Å and 3.167 Å, respectively, making them somewhat longer than those in **(2)**.

The hydrogen bonding exhibited by compound **(4)**, $\text{N}_3\text{P}_3\text{Cl}_2(\text{NHBU}^t)_4$, shows a similar dimer motif (Figure 8), though with a different conformation of the 8-membered ring, which is a boat-form with the phosphorus atoms at the apices and the central 6 atoms coplanar. The symmetric N...N distances, with a value of 3.392 Å, are even longer than in compound **(3)**, indicating weaker hydrogen bonding, which presumably arises from an increase in steric hindrance in the hydrogen bonding region.

Fig. 6,7,8

Steiner and co-workers (Bickley et al, 2003) reported no hydrogen-bonding in the crystal structure of $\text{N}_3\text{P}_3(\text{NHBU}^t)_6$ **(5)**. With the shortest N...N separation in the structure being 4.950 Å there is certainly no sign of a hydrogen bond from any $\text{BU}^t\text{N-H}$ to a ring nitrogen atom, as found in the three structures discussed above. There may be a very weak intramolecular interaction from one NHBU^t group to another NHBU^t in a cis non-geminal disposition, because there are two of these interactions having separations of 3.751 Å and 3.766 Å in chemically-identical environments in the two molecules comprising the asymmetric unit.

3.3. Structure - property relationships

The molecular parameters of compounds **(2)** - **(5)** are discussed in terms of the basicity of each molecule. The NHBU^t -substituent is one of the most base-strengthening primary amino residues so far investigated, with a substituent constant α_R -value of 5.9. (Feakins et al, 1969). The basicities of the more basic compounds, $\text{N}_3\text{P}_3(\text{NHBU}^t)_6$ and $\text{N}_3\text{P}_3\text{Cl}_2(\text{NHBU}^t)_4$, have been measured in nitrobenzene solution with values of 8.0 and 4.35, respectively (Feakins, Last &

Shaw, 1964). In fact the basicity of 8.0 for compound (4) would be about 9.9, if allowance is made for the saturation effect (Feakins et al, 1969). The basicity values of the remaining derivatives have been obtained by summation of known substituent basicity constants ($\Sigma\alpha_R$) according to the method previously described (Besli et al, 2002b), viz. -20.3, -14 and -8 for (1), (2) and (3), respectively. These $\Sigma\alpha_R$ values span a range of 30 pKa units.

3.3.1. Molecular structures

Although the preparation of compound (2) has been published on two occasions, different physical properties were reported; the first report (Das et al, 1965) gave a melting point of -10 to -11°C and later a ^{31}P NMR spectrum with absorptions at 16.0 and -5.3 ppm (Keat, Shaw & Woods, 1976). The sample of compound (2) prepared for this study has a melting point of 46°C and a ^{31}P NMR spectrum with absorptions at 21.1 and 13.45 ppm. As its structure is confirmed by X-ray crystallography (Figure 3), this indicates that the former report must have been incorrectly assigned to a different product. The second report (Begley, Sowerby & Bamgboye, 1979) gave a melting point of 110°C for compound (2), which may indicate a different polymorph, but in the absence of corroborating evidence, such as a crystal structure or an NMR spectrum, that question remains unanswered.

The electron-donating power of the NHBu^t group is demonstrated by the $\Delta(\text{P-N})$ values of compounds (2), (3) and (4), which are 0.027, 0.063 and 0.063 Å, respectively (Table 2). As indicated by the results above, a simple additive behaviour is not expected for endocyclic parameters. For compound (2), in particular, some of the electron-density appears to be diverted into lengthening the $\text{P}(\text{NHBu}^t)\text{-Cl}$ bond, which at 2.017 Å is considerably longer than the PCl_2 bonds in this compound. There are substantial changes in some bond angles, but again these are non-uniform, e.g. reduction in α .

In contrast to the non-uniform changes in endocyclic parameters, the exocyclic ones follow uniform and consistent trends. The effect of the electron-releasing capacity of the substituents on the average values of the P-Cl bonds and the Cl-P-Cl bond angles in the remaining PCl_2 groups are compared with the sum of the substituent basicity constants ($\Sigma\alpha_R$) in Table 4, where the structures of some related PPh_2 -derivatives have been included, viz., $\text{N}_3\text{P}_3\text{Cl}_4\text{Ph}_2$ (6) (Mani, Ahmed & Barnes, 1965) and $\text{N}_3\text{P}_3\text{Cl}_2\text{Ph}_4$ (7) (Mani, Ahmed & Barnes, 1966). In this series of compounds there is a good correlation between the increase in P-Cl bond length with an increase in $\Sigma\alpha_R$ as shown graphically in Figure 9a. Although the changes are small for the di-substituted compounds in this sequence, they are in keeping with the electron-supplying properties discussed above. For the tetra-substituted compounds the effects on the P-Cl bond lengths are rather larger, as expected, because the effects of four donor groups are spread over only two P-Cl bonds, whereas the effects of two donors are spread over four P-Cl bonds for the di-substituted derivatives. A similar explanation can

account for the concomitant decrease in Cl-P-Cl bond angles with $\Sigma\alpha_R$ (shown graphically in Figure 9a), which is expected from a lengthening of the P-Cl bonds.

Fig. 9 Table 4

The above linear relationships are mirrored in a number of other physical properties. In a study of the Faraday effect of some aminochlorocyclotriphosphazenes in CCl_4 solution, it was noted that in a plot of the number of amino substituents *vs* the molecular magnetic rotation, geminal derivatives gave a good straight-line relationship, whilst non-geminal derivatives showed positive deviations (Bruniquel et al, 1973). A possible explanation of these observations is that the former only depends on electron distributions within the plane of the N_3P_3 ring; whereas in the latter there is ample evidence from crystallographic data that there is an electron-transfer, which changes the parameters of substituents above and below this ring.

In this study a significant correlation has been observed between molecular parameters and ^{35}Cl NQR frequencies of PCl_2 groups of cyclophosphazene derivatives, perhaps because this technique deals with crystalline substances as does crystallography. It has been shown earlier that a linear relationship exists between ^{35}Cl NQR frequencies and the P-Cl bond lengths for Ph-derivatives (Keat et al, 1972). The frequencies for the NHBU^t -derivatives (**3**) and (**4**) have also been reported (Sridharan et al, 1980). It is found that such a relationship holds for the compounds reported in this study and that it extends to their Cl-P-Cl bond angles (Figure 9b). These results are also important because the observed linear correlations between molecular parameters and a physical parameter (^{35}Cl NQR frequency) for molecules in the solid state is mirrored in the analogous dependence on a physical parameter (sum of substituent basicity constants, $\Sigma\alpha_R$) for molecules in the solution state.

The structural data also permits some tentative conclusions to be drawn as to why there is a mono-, $\text{N}_3\text{P}_3\text{Cl}_5(\text{NHBU}^t)$, but no tris-derivative, $\text{N}_3\text{P}_3\text{Cl}_3(\text{NHBU}^t)_3$, because the successive substitutions of the cyclophosphazene moiety change molecular parameters, particularly the P-Cl bond lengths. There is now a good deal of evidence for a hydrogen abstraction/chloride ion elimination mechanism leading to a trigonal planar intermediate, which then reacts rapidly with any nucleophile present (Das et al, 1965; Ganapathiappan et al, 1987). The proposed mechanism for nucleophilic substitution at a phosphorus site bearing an NHBU^t group is shown in Figure 10. When $\text{X} = \text{Cl}$, which is electron-withdrawing, the proton abstraction by base is reversible, which was clearly shown by a D_2O shake-up in proton NMR spectroscopy to eliminate the N-H coupling in compounds (**3**) and (**4**). If $\text{X} = \text{NHBU}^t$, which is a strongly electron-supplying group, proton abstraction is irreversible and thus prevents isolation of the tris-derivative.

Fig. 10

3.3.2. Hydrogen bonding trends

Compounds (2), (3) and (4) form 8-membered ring hydrogen-bonded dimers, with the rings in a saddle-shape for (2) and (3) and a boat conformation for (4). The increase in average N...N distances for (2) 3.087, (3) 3.145 and (4) 3.392Å are probably due to steric crowding. There are no intermolecular hydrogen-bonds for (5), which is a result of the steric shielding of the potential acceptor nitrogen atoms in the cyclophosphazene core of the molecule.

The position of protonation of cyclophosphazene derivatives was originally deduced to be the ring N atoms from potentiometric studies (Feakins et al, 1964) and this was later proven by crystallography (Mani & Wagner, 1971; Shaw, 1976). These same N atoms are involved in the observed hydrogen-bonding patterns. However, the weakest base, (2), seems to form the strongest hydrogen-bonds and the strongest base, (5), does not form any intermolecular hydrogen-bonded interactions. Undoubtedly steric hindrance must be the cause, a conclusion supported by the geometric and conformational results (*vide supra*) regarding the relative conformations of the NHBu^t groups.

4. Conclusions

This is the first series of products from reaction of N₃P₃Cl₆ with a given amine (in this case a bulky primary amine, H₂NR), where all the compounds have been characterised crystallographically. The three hydrogen-bonded dimers show two types of 8-membered ring conformation; one is saddle-shaped with slightly different hydrogen-bridges for N₃P₃Cl₅(NHBu^t) and N₃P₃Cl₄(NHBu^t)₂, whereas for N₃P₃Cl₂(NHBu^t)₄ the two intermolecular hydrogen-bonded bridges are identical and the conformation is that of a boat. The changes in observed molecular parameters show good correlation with changes in other physical properties such as the substituent basicity constants, the Faraday effect, some ³¹P NMR parameters and ³⁵Cl NQR frequencies. In spite of the much increased basicity of the ring nitrogen atoms, the capacity for intermolecular hydrogen-bonding decreases from the mono-substituted compound, N₃P₃Cl₅(NHBu^t), to N₃P₃Cl₂(NHBu^t)₄ and it has disappeared altogether for N₃P₃(NHBu^t)₆. This behaviour is attributed to steric hindrance. The change in molecular parameters with increasing replacement of Cl atoms by NHBu^t groups gives rise to regular changes for exocyclic parameters, but is somewhat erratic for endocyclic parameters because of the different degrees and positions of substitution.

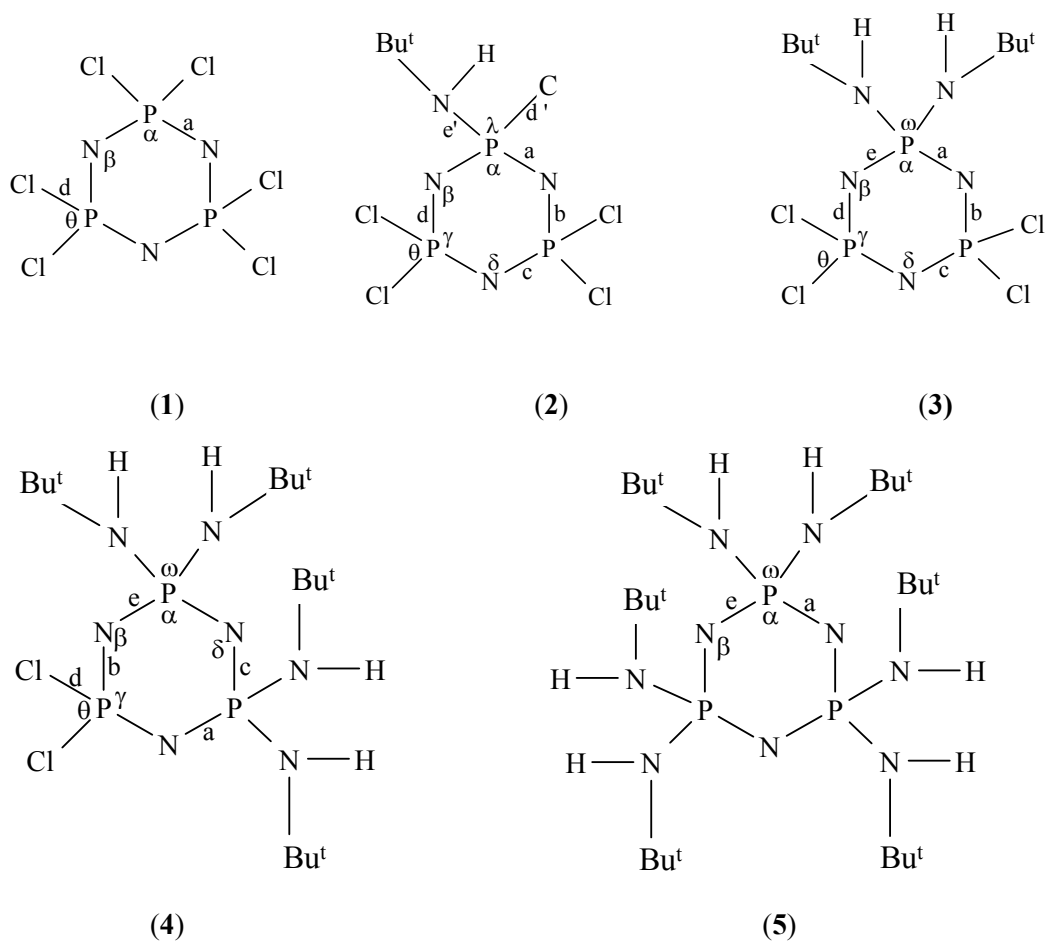


Figure 1 Designation of molecular parameter descriptors for compounds (1) - (5)

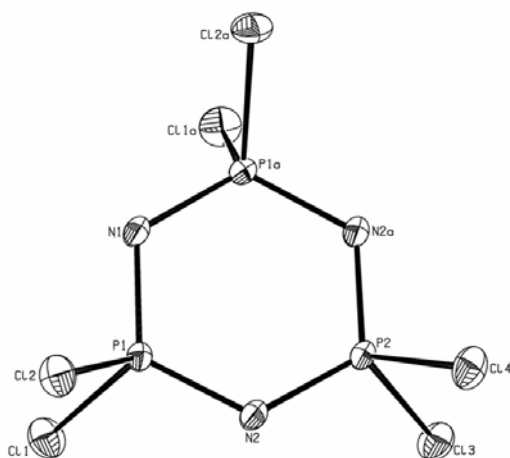


Figure 2 The molecular structure and numbering scheme of (1)

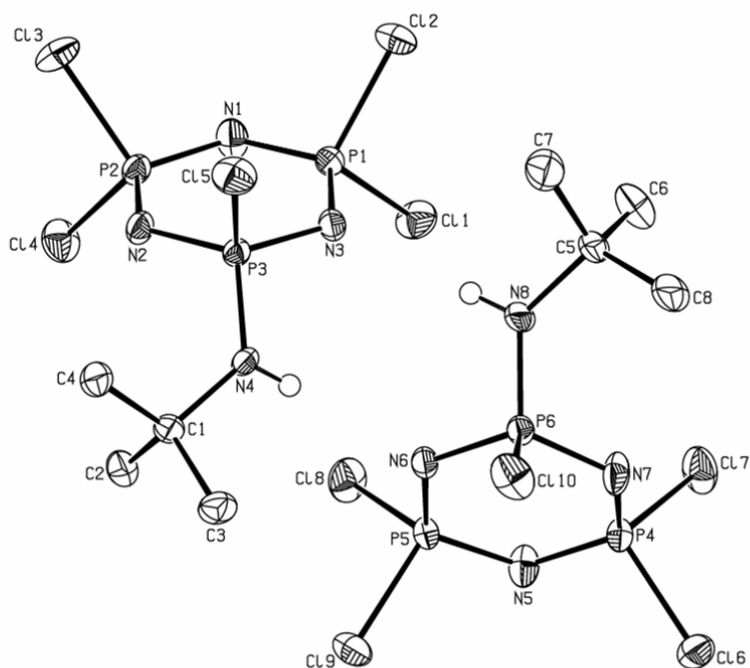


Figure 3 The molecular structure and numbering scheme of compound (2)

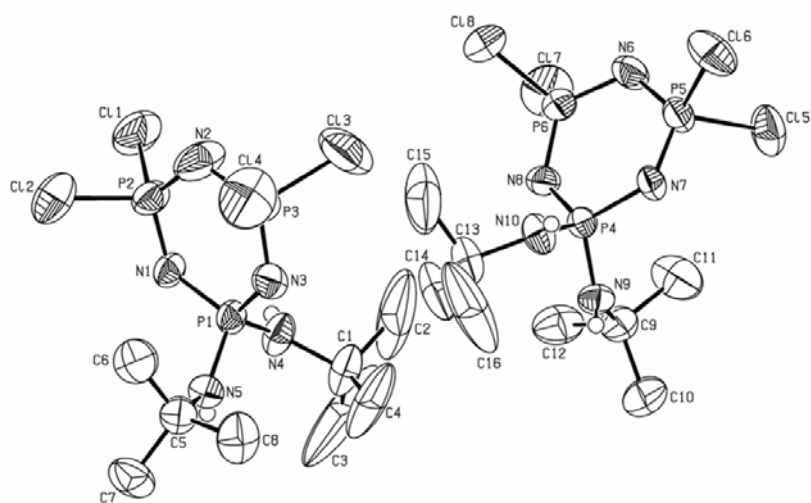


Figure 4 The molecular structure and numbering scheme of compound (3)

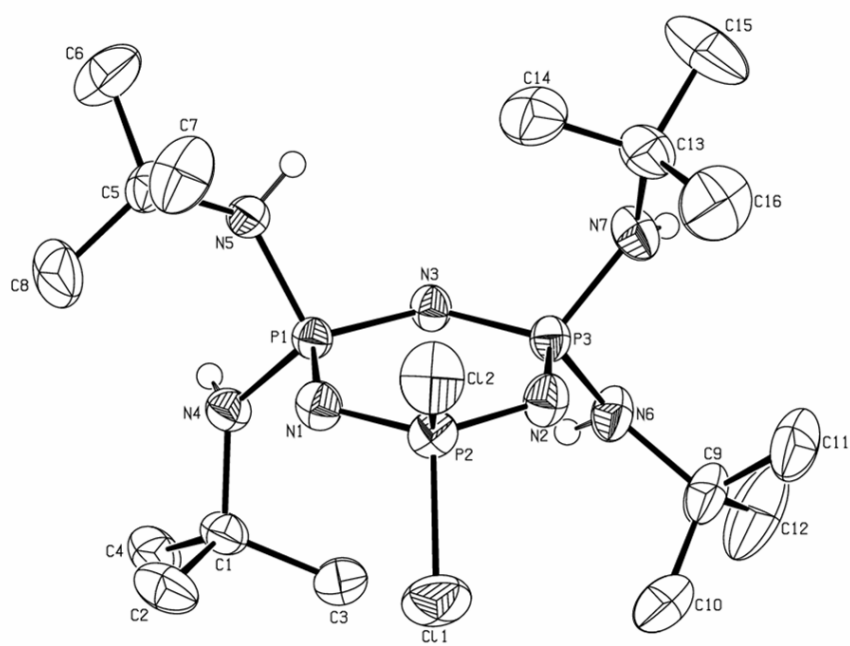


Figure 5 The molecular structure and numbering scheme of compound (4)

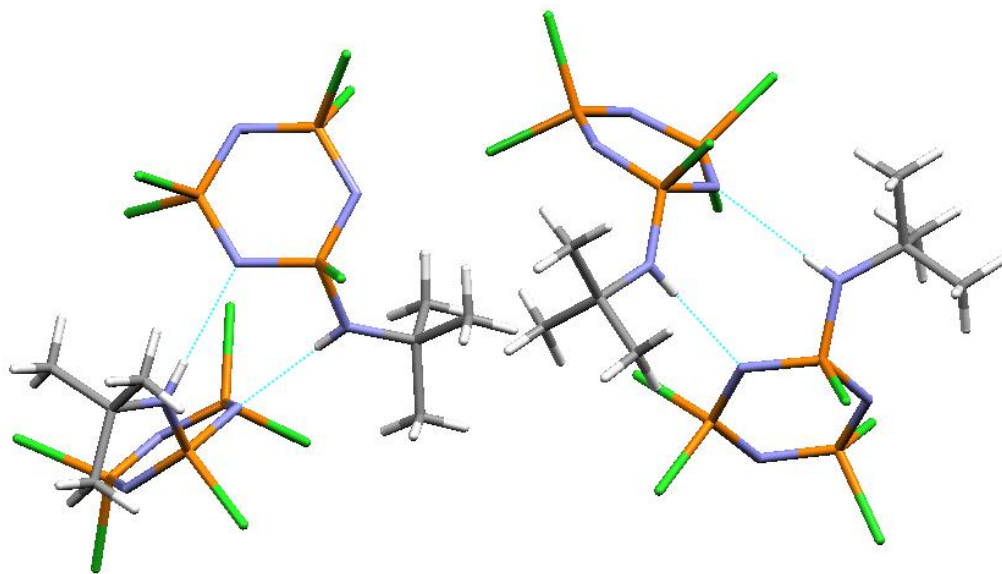


Figure 6 The hydrogen bonded structure formed by (2)

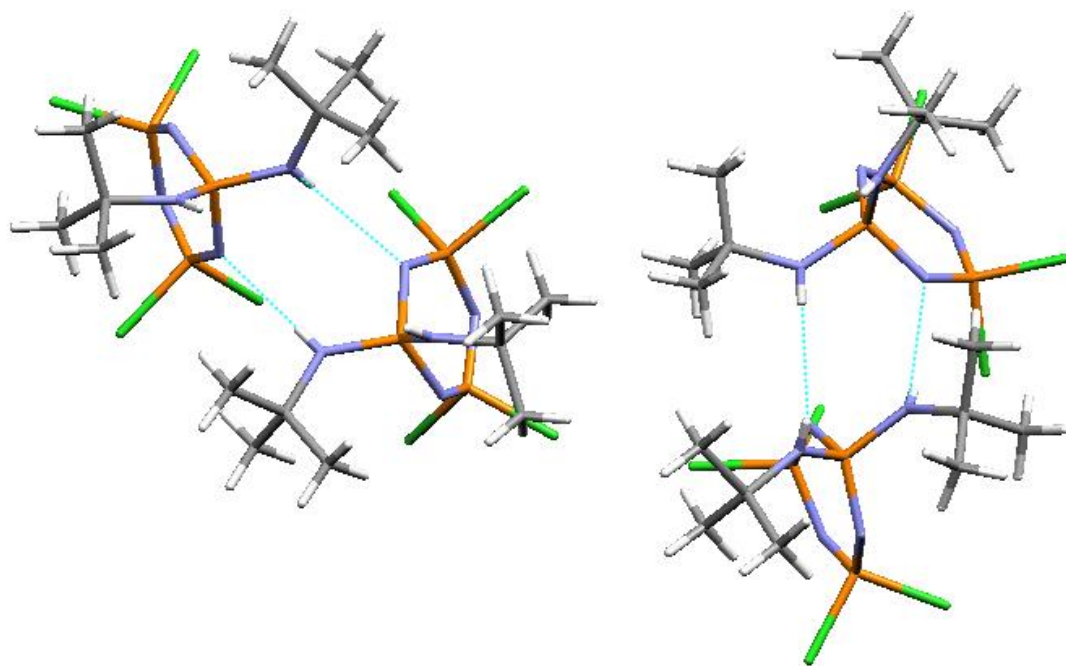


Figure 7 The hydrogen bonded structure formed by (3)

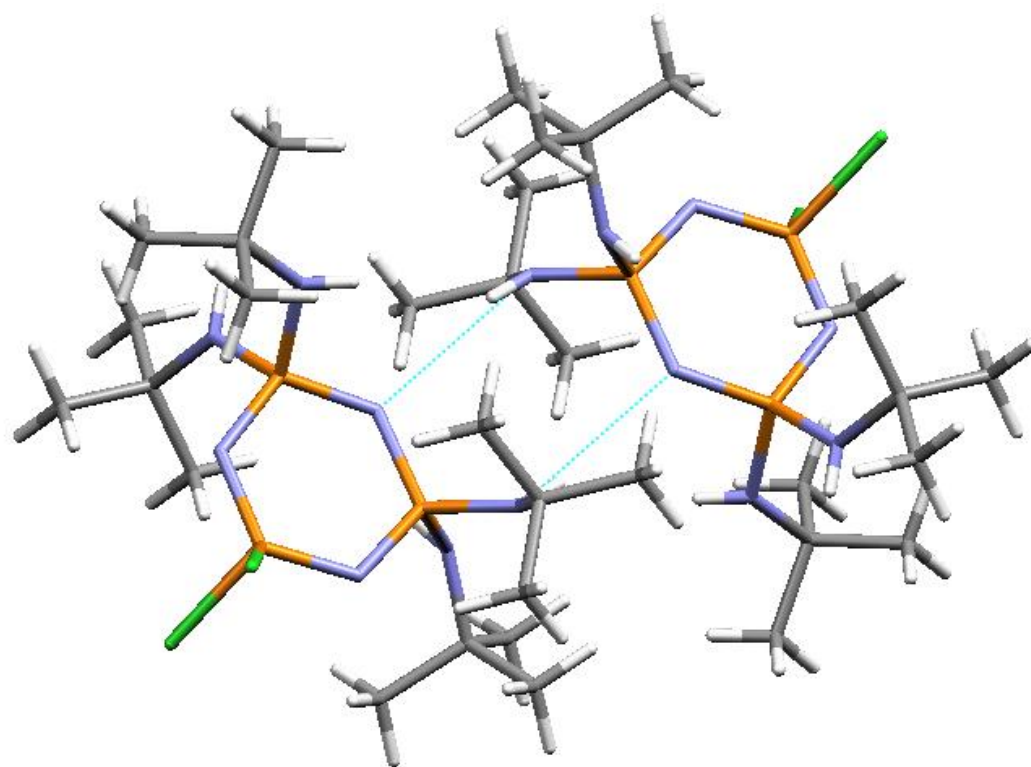
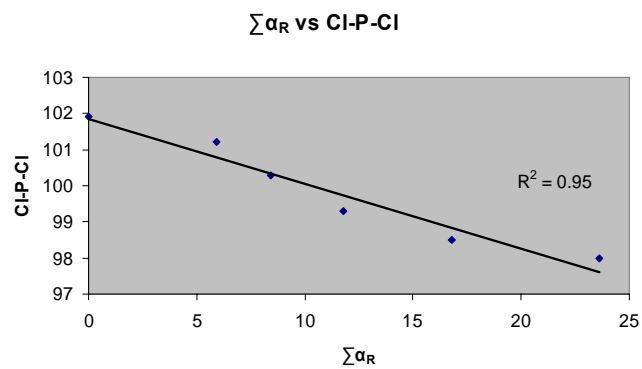
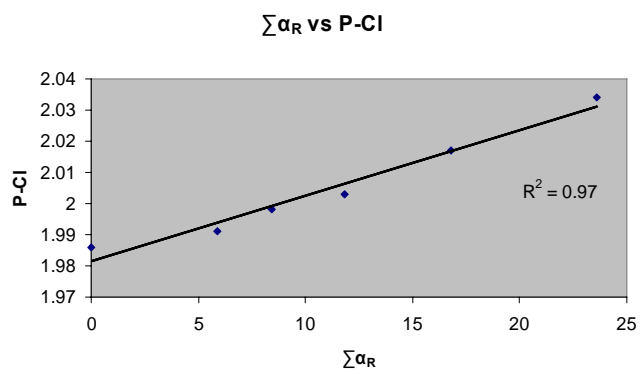
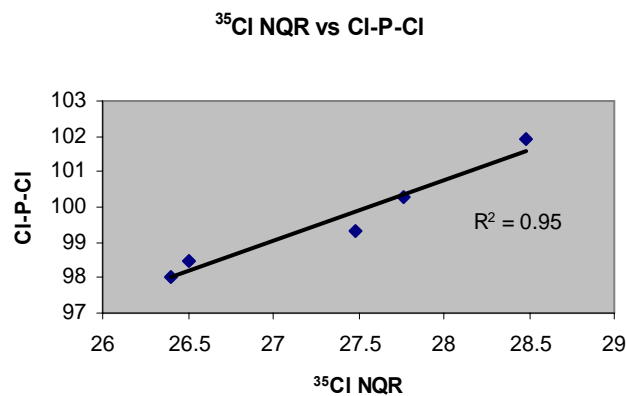
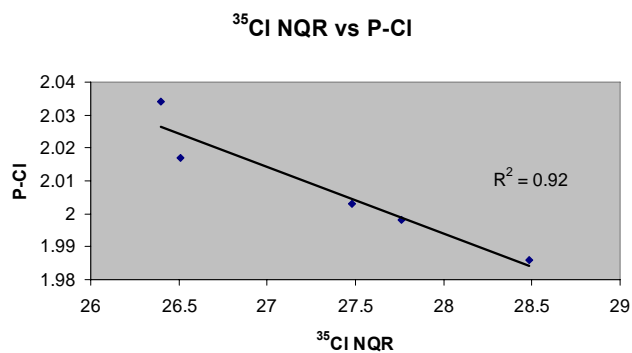


Figure 8 The hydrogen bonded structure formed by (4)



a)



b)

Figure 9 Correlation between a) sum of substituent basicity constants ($\Sigma\alpha_R$) and b) averaged ^{35}Cl NQR frequencies (MHz) for P-Cl bond length and Cl-P-Cl bond angle respectively, for data presented in Table 4.

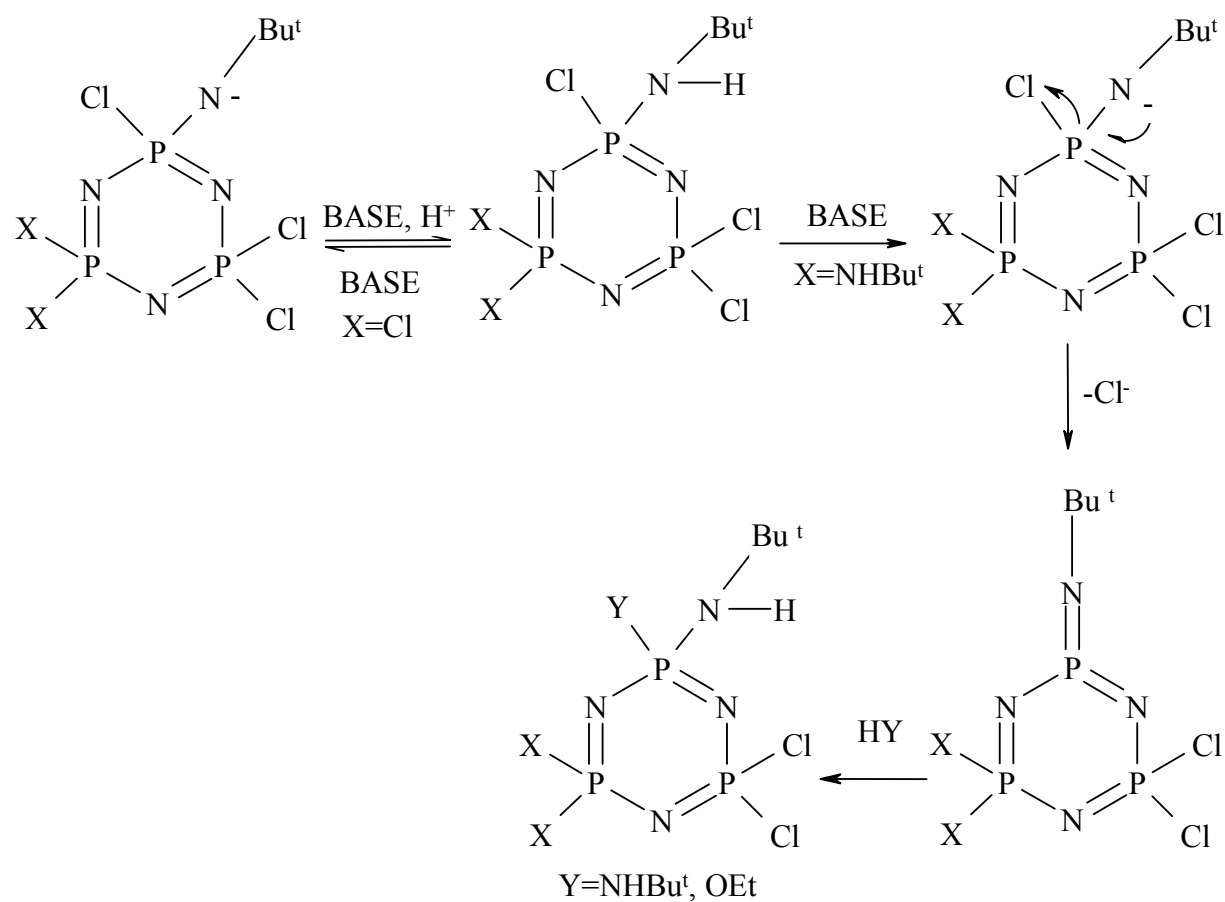


Figure 10 Proposed mechanism for nucleophilic substitution at a phosphorus site bearing an NHBu^t group.

Table 1 Data collection and refinement parameters for structures (1) - (4)

	1	2	3	4
Empirical formula	N ₃ P ₃ Cl ₆	C ₄ H ₁₀ Cl ₅ N ₄ P ₃	C ₈ H ₂₀ Cl ₄ N ₅ P ₃	C ₁₆ H ₄₀ Cl ₂ N ₇ P ₃
Formula weight	347.64	384.32	421.00	494.36
Crystal system	Orthorhombic	Monoclinic	Orthorhombic	Monoclinic
Space group	<i>Pnma</i>	<i>P2₁/c</i>	<i>Pna2₁</i>	<i>P2₁/n</i>
a (Å)	13.8572(8)	13.8045(14)	20.3441(7)	12.5207(2)
b (Å)	12.8086(11)	10.7964(16)	11.9481(4)	16.1282(2)
c (Å)	6.0801(5)	20.7719(12)	15.9661(7)	13.1311(2)
β (°)	90	104.132(7)	90	95.9030(10)
Volume (Å ³)	1079.17(14)	3002.1(6)	3880.9(3)	2637.59(7)
Z	4	8	8	4
Density (calc) Mg/m ³	2.140	1.701	1.441	1.245
Crystal size (mm)	0.5 × 0.4 × 0.1	0.18 × 0.10 × 0.02	0.16 × 0.14 × 0.06	0.40 × 0.25 × 0.25
Independent reflections	1283	6867	8590	5994
R(int)	0.0218	0.0437	0.0785	0.0566
Final R indices $F^2 > 2\sigma F^2$	R1 = 0.0275	R1 = 0.0339	R1 = 0.0565	R1 = 0.0382
	wR2 (all) = 0.0735	wR2 (all) = 0.0862	wR2 (all) = 0.1416	wR2 (all) = 0.1003
Δρ max / min (eÅ ⁻³)	0.671 / -0.685	0.486 / -0.498	0.610 / -0.569	0.270 / -0.334

Table 2 Selected molecular parameters for structures (1) - (5)^a

	(1)	(2)	(3)	(4)	(5)
a	1.577	1.594	1.619	1.623	1.578
b		1.567	1.556	1.560	
$\Delta(\text{P-N}) = \text{a-b}$		0.027	0.063	0.063	
c		1.575	1.577	1.598	
d	1.986	1.991	2.003	2.034	
d'		2.017			
e			1.616	1.635	1.638
e'		1.600			
α	118.5	116.9	112.3	114.4	115.9
β	121.1	121.6	123.5	121.9	121.9
γ		119.2	119.9	121.9	
δ		120.6	118.4	126.7	
θ	101.9	101.2	99.3	98.0	
ω			104.8	102.5	101.7
λ		107.4			
ΣN		358.3	358.8	353.7	355.1

^a The definition of each molecular parameter for compounds (1) - (5) is summarised diagrammatically in figure 1

Table 3 Geometric parameters for NH-Bu^t groups

Compound		Torsional angles of NHBu ^t substituents to both adjacent ring N atoms		C...C separations between central atoms on adjacent NHBu ^t groups
(2)	Molecule A	31.93	162.50	
	Molecule B	-41.14	-171.54	
(3)	Molecule A	41.06 49.21	-82.41 172.74	4.720
	Molecule B	-37.58 -50.16 86.81	-174.32	4.675
(4)	Molecule A	-43.07	84.83	4.741
		-42.17	85.23	4.747
		-37.63	-162.53	
		-32.43	-158.29	
(5)	Molecule A	-63.84	79.70	4.579
		-63.85	-83.88	4.605
		-51.52	83.18	4.548
		59.28	170.73	
		45.75	171.70	
		-45.32	-173.10	
	Molecule B	59.80	-81.27	4.575
		-63.30	84.54	4.569
		-60.85	169.13	4.554
		-49.67	172.77	
		48.31	173.10	
		79.12 -45.01		

Table 4 Sum of substituent basicity constants ($\sum a_R$), geometric parameters and averaged ^{35}Cl NQR frequencies of the PCl_2 group of compounds (1) - (4), (6) and (7)^a

Compound	Molecular formula	P-Cl / (Å)	Cl-P-Cl / (°)	$\sum a_R$	Averaged ^{35}Cl NQR Frequencies (77K) /MHz
(1)	$\text{N}_3\text{P}_3\text{Cl}_6$	1.986	101.9	0.0	28.482
(2)	$\text{N}_3\text{P}_3\text{Cl}_5(\text{NHBut})$	1.991	101.2	5.9	
(6)	$\text{N}_3\text{P}_3\text{Cl}_4\text{Ph}_2$	1.998	100.3	8.4	27.759
(3)	$\text{N}_3\text{P}_3\text{Cl}_4(\text{NHBU}^t)_2$	2.003	99.3	11.8	27.481
(7)	$\text{N}_3\text{P}_3\text{Cl}_2\text{Ph}_4$	2.017	98.5	16.8	26.511
(4)	$\text{N}_3\text{P}_3\text{Cl}_2(\text{NHBut})_4$	2.034	98.0	23.6	26.398

^a Compounds $\text{N}_3\text{P}_3\text{Cl}_4\text{Ph}_2$ (6) and $\text{N}_3\text{P}_3\text{Cl}_2\text{Ph}_4$ (7) are included for comparison purposes.

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