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Novel cyclophosphazene monomers and their polymerization behavior

Bosscher, Gerard; Hadziioannou, G

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Chapter 1

INTRODUCTION

1.1 Phosphazenes

Cyclic and linear phosphazenes (Fig. 1.1) are characterized by a repeating unit $-\text{[N=PR}_2\text{]}_n-$ in which nitrogen is trivalent and phosphorus pentavalent. Ring sizes for the cyclic derivatives vary from three to about forty repeating units whereas for the linear polyphosphazenes derivatives are known which contain up to 15000 repeating units [1,2].

The chemistry of the phosphazenes goes back to 1834 when Liebig and Wöhler isolated a small amount of an unidentified crystalline product from the reaction of ammonia and phosphorus pentachloride [3]. In 1864 Gladstone and Holmes showed the molecular formula to be $(\text{NPCl}_2)_3$ [4,5]. In 1895 Stokes suggested a cyclic structure for this compound [6]. He also studied substitution and hydrolysis reactions of chlorocyclophosphazenes [7-10]. Furthermore he reported about the thermal polymerization of chlorocyclophosphazenes, resulting in the first 'inorganic' rubber [8].

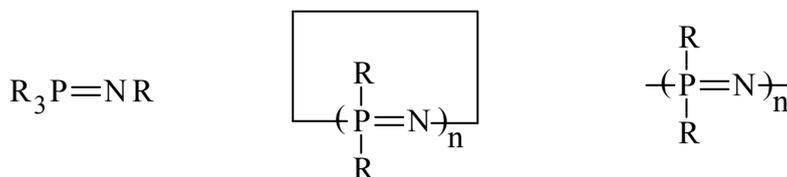


Figure 1.1 Structures of some phosphazenes

It was not until the 1950s that the growing demand for materials with new and unusual properties led to an enormous increase in the research on substitution and polymerization reactions of phosphazenes [11]. In the 1960-70s van de Grampel and co-workers introduced a series of mixed ring systems with one or more of the PCl_2 centres replaced by a SOR group (Fig. 1.2) [12-14]. These structures are known as cyclothiaphosphazenes.

As the knowledge of the chemistry increased scientific interest shifted towards possible use in a wide range of applications in fields such as: medicine, flame retardancy and

microlithography [15-28]. Several reviews on phosphazenes with recent literature are available [29-34].

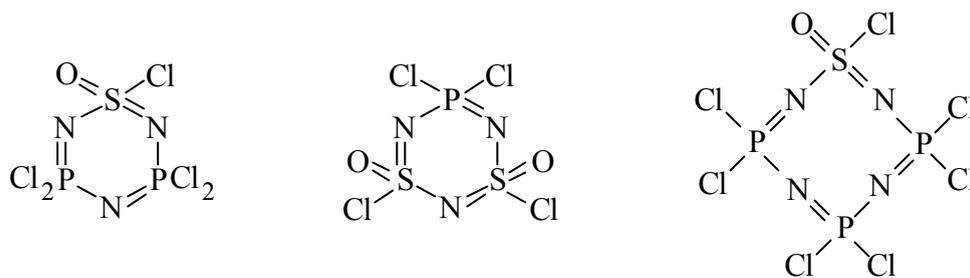


Figure 1.2 Structures of some cyclothiaphosphazenes

1.2 Structure and reactivity of phosphazenes

1.2.1 Bonding

The first X-ray structural data on polyphosphazenes were provided by Meyer, Lotmar and Pankow in 1936 who studied the chain-repeating distance of $(\text{NPCl}_2)_n$. From this value they calculated for the P-N bond distance a value of 1.7-1.8 Å and for the Cl-P-Cl angle a value of 102° [35]. Recent structural studies on poly(dichlorophosphazene) suggest alternation in P-N bond lengths in the polymer backbone with values of 1.67(8) and 1.44(5) Å [36]. However, the difference between these bond lengths border to significance. For the Cl-P-Cl bond angle a value of 99° was found [36]. For the polymer $(\text{NPMe}_2)_n$ no alternation effect is observed [37]. It should be noted that in the case of polymers the scarce number and quality of diffraction data makes it difficult to determine accurate bond lengths.

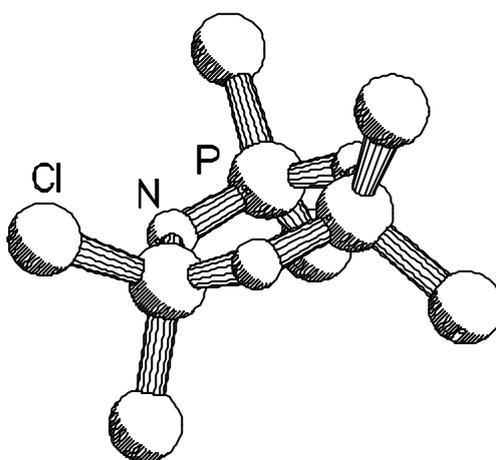


Figure 1.3 Molecular structure of hexachlorocyclotriphosphazene

An enormous amount of structural data for cyclophosphazenes is available and is still increasing. For homogeneously substituted cyclotriphosphazenes bond equality is observed around the nearly planar ring skeleton. Considering for instance $(\text{NPCl}_2)_3$, the geometry at the phosphorus atom is almost tetrahedral (sp^3) whereas the hybridization at the nitrogen approaches a sp^2 character (Fig. 1.3) [38]. The P-N bond length of 1.58 Å is considerable shorter than the so-called single P-N bond in $(\text{H}_3\text{N-PO}_3)^-$ (1.77 Å) [39].

In heterogeneously substituted cyclophosphazenes, e.g. $(\text{NPCl}_2)_2\text{NP(alkyl)}_2$, the $\text{P(alkyl)}_2\text{-N}$ bond length in the $\text{P(alkyl)}_2\text{-N-PCl}_2$ segment is larger than 1.58 Å while the $\text{PCl}_2\text{-N}$ bond is shorter. The P-N bond distances in the $\text{PCl}_2\text{-N-PCl}_2$ segment are within the experimental error not different from each other, and equal to about 1.58 Å. Representative examples of this kind of structures are given in Chapter 3 of this Thesis.

Several theories of bonding have been presented to explain the observed structural properties in cyclophosphazenes of which the $d_\pi\text{-p}_\pi$ bonding model is the most widely adopted [11]. This model developed by Craig and Paddock and by Dewar, Lucken and Whitehead describes the bonding between the phosphorus and nitrogen atoms in terms of σ bonding and additional π bonding arising from the overlap of 3d orbitals of the phosphorus with nitrogen p orbitals [40-42]. The tendency of a phosphorus centre towards π bonding depends on the electron withdrawing capacity of the ligands attached to it. The larger the electronegativity of the substituent the greater the degree of π bonding at the phosphorus. This means that in an inhomogeneously substituted PNP segment the P-N bond to the more electronegative phosphorus centre is shortened, whereas the other is elongated. Following the same reasoning one should expect that in an equally substituted PNP segment the P-N bond lengths are the same. Indeed, this is observed in X-ray determination studies on heterogeneously substituted cyclophosphazenes. Recent theoretical molecular orbital calculations support the concept that the phosphorus 3d orbitals contribute to the endocyclic π bonding [43,44].

1.2.2 Reactivity towards nucleophiles

Probably the most studied nucleophilic substitution reaction on cyclophosphazenes is the substitution of chlorines by amines [11,31,32]. The aminolysis takes place according to two pathways, a geminal (substitution on the same P atom) and a non-geminal one (different P atoms), depending on amine, solvent and stage of substitution.

The replacement of halogens can also easily be performed with reagents as alcohols (or alcoholates) and thiols (or thiolates). Substitution by alcohols and phenols proceed in general via a non-geminal pathway, while thiolates are found to react in a geminal pathway [11,32].

Reactions of organometallic reagents with phosphazenes result in derivatives in which the substituents are linked to the phosphorus by phosphorus-carbon bonds. These bonds are less reactive than P-O bonds which can undergo rearrangements (see also Section 1.2.3) [11,32,45]. Initially, reactions of $(\text{NPCl}_2)_3$ with organolithium and -magnesium reagents were carried out in diethyl ether or dioxane. However, extensive ring degradation was observed [11,46,47]. In contrast to these observations, analogous reactions with $(\text{NPF}_2)_3$ yielded a large variety of cyclic compounds with alkyl, alkenyl and aryl substituents in high yields [11,48-50]. The problem of skeletal bond cleavage in reactions with chlorocyclophosphazenes and Grignard reagents was solved in 1979 by Allcock et al.. He reported the reaction of $(\text{NPCl}_2)_3$ with a Grignard reagent in tetrahydrofuran in the presence of $[\text{}^n\text{Bu}_3\text{PCuI}]_4$. This resulted in the formation of a copper(I)phosphazene complex via a so-called metal-halogen exchange mechanism. Treatment of this reactive intermediate with 2-propanol yielded a gem-hydridoalkylphosphazene [51]. Originally, Allcock proposed for the complex a structure in which a copper atom is coordinated to the ring nitrogen, whereas a chlorine is replaced with an organic group. In solvents with a low coordinative ability these intermediates are not stabilized resulting in ring degradation.

Formation of a copper complex does not take place with fluoro derivatives. The electron withdrawing effect of the electronegative fluor atoms lowers the electron density at the ring nitrogen to such an extent that coordination at the ring nitrogen is not longer possible. Instead a direct nucleophilic substitution path is followed.

Later the reaction of copper(I) assisted Grignard reagents with $(\text{NPCl}_2)_3$ was extended by Buwalda et al., who used the metallophosphazene in reactions with ketones and aldehydes to give a gem-diorganophosphazene and geminal substituted alkyl(hydroxyalkyl) derivatives [52,53]. Based on ^{31}P NMR data Buwalda et al. proposed the following structure (see Fig. 1.4) for the metallophosphazene intermediate, which structure is now widely adopted [53].

In 1983 Allcock et al. showed that without $[\text{}^n\text{Bu}_3\text{PCuI}]_4$ the reaction of a Grignard reagent with $(\text{NPCl}_2)_3$ in tetrahydrofuran results in the formation of substituted cyclophosphazenes [54]. Mixtures of monoalkylphosphazene and bi(cyclophosphazene) could be obtained in high yields without ring cleavage. The ratio of the products depends on the nature of the Grignard reagent and reaction temperature applied. For this reaction also a metal-halogen exchange process seems to be operative.

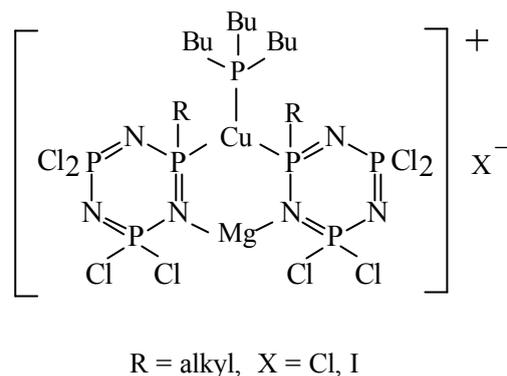
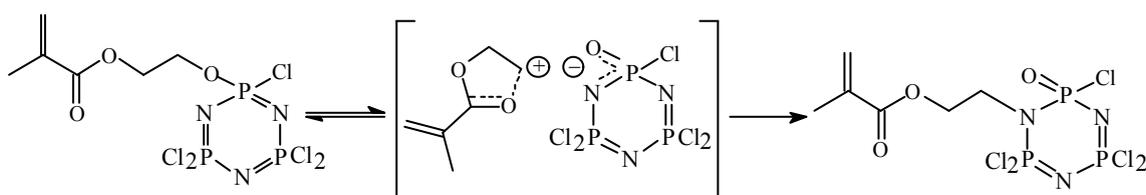


Figure 1.4 Structure of a copper(I)phosphazene intermediate

1.2.3 Stability of alkoxy cyclophosphazene derivatives

Cyclophosphazenes are known to undergo ligand migration reactions under certain conditions [11,32,45].

Some alkoxy cyclophosphazenes can rearrange to phosphazanes via the irreversible migration of the alkyl group from the oxygen atom to the γ -ring nitrogen. These thermal rearrangement reactions are catalyzed by alkyl halides. The rearrangement process observed for the (2-oxyethyl methacryl) phosphazene, which even takes place at ambient temperatures, has been studied in detail (Scheme 1.1) [45]. Dissociation of the alkoxy group into an ion pair and subsequent attack of the ring nitrogen at the stabilized carbocation finally generates the phosphazane.



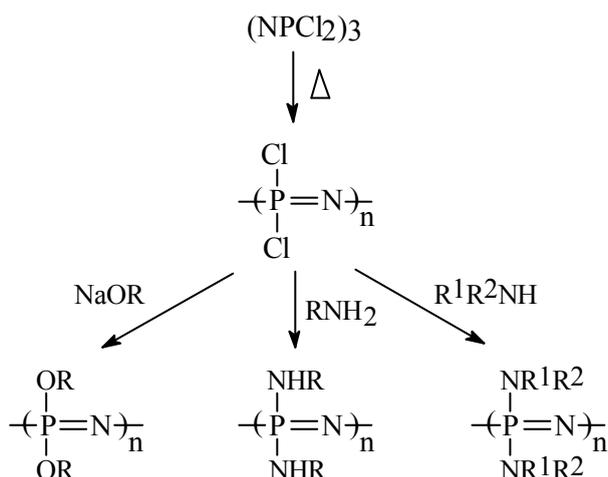
Scheme 1.1 Rearrangement of an alkoxyphosphazene to a phosphazane as proposed by Hayes and Allen [45]

Apart from the rearrangement reactions exchange reactions can occur. When performing substitution reactions exchange between organic groups at the phosphorus is observed in some cases. For instance, when $\text{N}_3\text{P}_3(\text{OC}_6\text{H}_4\text{NO}_2)_6$ is reacted with sodium trifluoroethoxide in tetrahydrofuran at 65°C , $\text{N}_3\text{P}_3(\text{OCH}_2\text{CF}_3)_6$ is obtained [11].

1.3 Phosphazenes and polymers

1.3.1 Polyphosphazenes

Initially, the thermal ring-opening polymerization of $(\text{NPCl}_2)_3$ resulted in the formation of a hydrolytically unstable, highly cross-linked material that could not be processed further. In 1966 Allcock, Kugel and Valan succeeded in the controlled synthesis of the high molecular, linear poly(dichlorophosphazene) $(\text{NPCl}_2)_n$, which appeared to be soluble in various anhydrous organic solvents [2,55]. The solubility combined with the high reactivity of the PCl_2 groups, enabled them to convert the polymer by a wide variety of nucleophiles to a large variety of organo-substituted polyphosphazenes (Scheme 2.1). In contrast to $(\text{NPCl}_2)_n$ the replacement of chlorine with suitable groups results in hydrolytically stable polymers [11,30,55].



Scheme 1.2 Reaction scheme for the synthesis of poly(diorganophosphazenes)

As can be seen in Scheme 1.2 substitution reactions on $(\text{NPCl}_2)_n$ are in general carried out with alcoholates and amines. Halogen replacement in $(\text{NPCl}_2)_n$ and $(\text{NPF}_2)_n$ by treatment with organometallic reagents is accompanied with competing side reactions as skeletal cleavage and cross-linking [46,56,57]. The synthesis of poly(diorganophosphazenes) with all substituents linked to the polymer backbone by a direct P-C bond is therefore not possible via this route.

In another approach $(\text{NPCl}_2)_3$ is allowed to react first with the organometallic reagent by reactions discussed earlier in Section 1.2.2. The partly organo-substituted cyclic trimer can then be converted to a high polymer in a similar manner as $(\text{NPCl}_2)_3$. As an example serve the non-

geminally substituted chlorocyclophosphazene derivatives, $(\text{NCl}_2)(\text{NPClMe})_2$ and $(\text{NPClMe})_3$, which are capable to undergo thermal ring opening polymerization [58]. However, fully substituted cyclophosphazenes as $(\text{NPMe}_2)_3$ or $(\text{NPh}_2)_3$ undergo ring-ring equilibration reactions but polymers are not obtained [58,59].

An alternative method for the synthesis of polyphosphazenes has been developed by Neilson and Wisian-Neilson involving thermal polycondensation of N-silylphosphoranimines [60,61]. An example is given in Scheme 1.3. The polymers thus prepared have lower molecular weights than those synthesized by the route outlined in Scheme 1.2. However, the advantage of this procedure is that it leads to poly(diorganophosphazenes) with all groups attached to the polymer backbone by direct phosphorus-carbon linkages.



Scheme 1.3 Alternative synthesis method for poly(diorganophosphazenes)

Recently the ring-opening polymerization of the mixed ring systems $(\text{NCl}_2)_2\text{NSCl}$, $(\text{NCl}_2)_2\text{NSOCl}$ and $(\text{NCl}_2)_2\text{NSOF}$ have been reported [62-64]. The thermal ring-opening polymerization of the mixed rings takes place at much lower temperatures compared with $(\text{NCl}_2)_3$. For the mixed ring systems the required temperatures range from 90 to 180 °C whereas for $(\text{NCl}_2)_3$ a temperature of 250 °C is needed. The chlorine atoms in these polymers can also be replaced by various nucleophiles, which means that these polymers stand at the basis of a whole new class of inorganic polymers.

1.3.2 Poly(alkenylcyclophosphazenes)

Allen and co-workers developed another important entry to the polymer chemistry of cyclophosphazenes. Their approach involves the synthesis of cyclophosphazenes with an unsaturated moiety and subsequent radical copolymerization with various organic monomers, e.g. styrene or methyl methacrylate [22,65-67]. In contrast to the polyphosphazenes, the hybrid inorganic-organic polymers thus obtained consist of an organic backbone with the inorganic ring as pendant group. Synthesis of these polymers offers the possibility to transfer advantageous properties of inorganic components to traditional organic polymers.

By introducing an insulating group between double bond and phosphazene ring the influence of the ring can be minimized. An example of a monomer with a spacer is given in Scheme 1.4, 2.

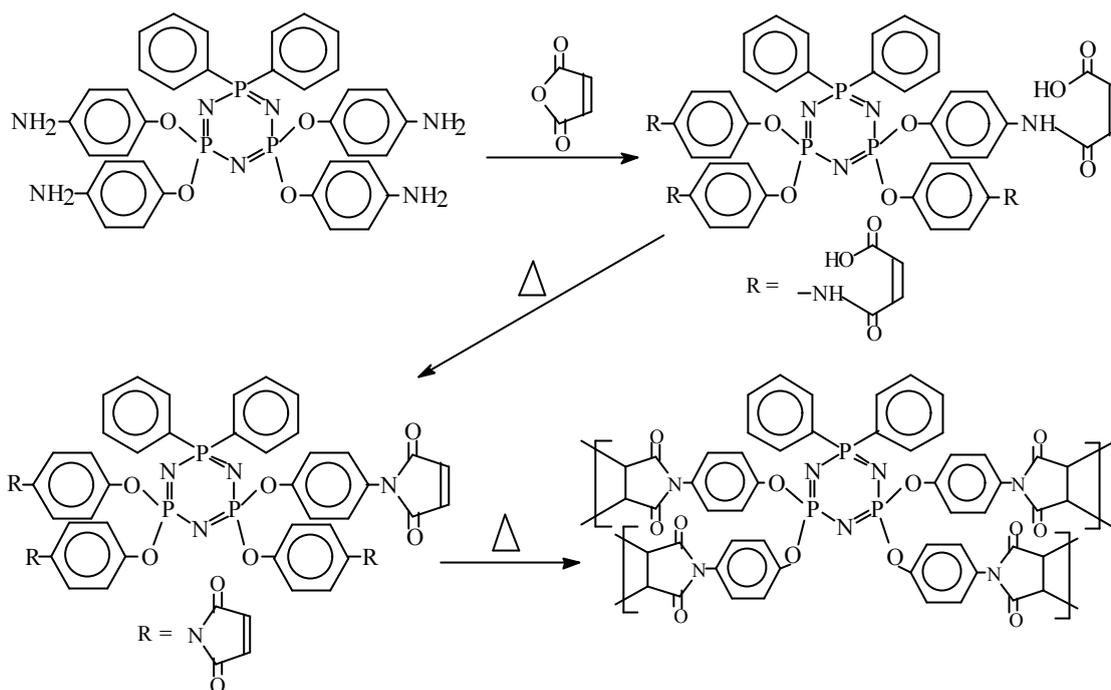
1,1-Disubstituted alkenes form another class of monomers (Scheme 1.4, 3). Here the negative electronic effect of the phosphazene is counterbalanced by a group with an electron donating capacity. Although this method is less effective than the use of a spacer group, the largest disadvantage of this type of monomer lies in the fact that ceiling temperatures for these compounds are in general lower than the reaction temperatures used in normal radical-initiated polymerizations. As a result these monomers are only capable to copolymerization reactions.

1.3.3 Cycloliner and cyclomatrix organophosphazenes

The multifunctionality and reactivity of the chlorocyclophosphazenes makes them very suitable for the synthesis of cycloliner and cyclomatrix polymer resins. In particular, the group of Kumar and Gupta is active in this field and has developed several interesting phosphazene derivatives. Their basic starting compound for these materials consists of an aminophenoxy substituted cyclophosphazene. With two of these substituents on the ring, linear polyimide polymers can be obtained when the diamine compound is reacted with a dianhydride and subsequent cyclodehydration of the resulting polymer [69]. These phosphazene containing polyimide polymers showed a good thermo-oxidative stability and have a high char yield of 50-60% in air at 800 °C. In contrast with this, commercial linear polyimides degrade very rapidly in an air atmosphere beyond 600 °C without leaving any residue.

Cyclomatrix polymer resins (Scheme 1.5) are formed when the phosphazene ring, substituted with three or more of the aminophenoxy groups, is allowed to react with maleic anhydride. After cyclodehydration and polymerization of the maleimides a cyclomatrix material is formed, which had char yields of 60-70% at 700 °C in air [70,71].

Also soluble poly(ether imide) copolymers can be obtained via the “nitro displacement” polymerization [72]. According to this method a mixture of a nitrophthalimidophenoxy substituted cyclotriphosphazene and a bis(nitrophthalimido)-diphenyl ether is allowed to react with the disodium salt of bisphenol A [73]. The resulting copolymer has a molecular weight of 7×10^3 and shows a char yield of 30% at 700 °C in air.



Scheme 1.5 Formation of a phosphazene containing cyclomatrix polymer resin

1.4 Aim and survey of this thesis

Primarily, the goal of this study is the synthesis of chlorocyclophosphazene derivatives with an olefinic group directly attached to the ring by a P-C bond. Secondly, the reactivity of the novel phosphazene monomers in radical homo- and copolymerization reactions is examined. The observed polymerization behavior is related to the structure of the inorganic component. Finally, the thermal properties of the polymers prepared are investigated by means of thermogravimetric analyses (TGA), differential scanning calorimetry (DSC) and X-ray photoelectron spectroscopy (XPS). The flame retardant capacity of the phosphazene containing polymers is investigated in a qualitative way.

In Chapter 2 the synthesis of a styrene (STP), vinyl acetate (VAcP) and propene (PP) derivative is described along with some interesting and unexpected by-products. In the STP monomer a benzyl group isolates the olefin functionality from the electronegative phosphazene ring. In the case of VAcP and PP the phosphazene ring is directly bonded to the carbon atom of the double bond. Substitution of the remaining PCl_2 groups in STP and PP is easily accomplished by dimethylamine.

Chapter 3 discusses in more detail the crystal structures of some of the phosphazene derivatives described in Chapter 2. Among them is the first known example of a carbon-bridged bicyclotriphosphazene.

Chapter 4 deals with the radical (co)polymerization behavior of the monomers presented in Chapter 2. Reactivity ratios are calculated by using the Kelen-Tüdös method and a computer program based on a new iterative linear least-squares method. In the case of STP the benzyl group acts as a very effective spacer. This means that STP shows a reactivity comparable with that of styrene. The observed polymerization behavior of the 1,1-disubstituted alkenes, VAcP and PP, is greatly influenced by the presence of two substituents on the same carbon atom of the double bond. These groups induce a large steric hindrance at the polymer chain end.

Chapter 5 describes the thermal behavior of the hybrid inorganic-organic polymers derived from the phosphazene monomers. From TGA experiments it is shown that the thermal degradation process of the various copolymers proceeds in one or two steps. From XPS studies on samples after the first and second weight loss step, several degradation processes can be discerned. These processes are: depolymerization, elimination of HCl and degradation of the phosphazene ring. The homopolymer of the styrene derivative STP shows only one weight loss step. It is assumed that in this case the above mentioned processes proceed simultaneously. The observed char yields for the copolymers increase with higher phosphazene contents.

1.5 Nomenclature

The nomenclature of the phosphazene ring systems has been described in detail by de Ruiter [74]. As the use of the IUPAC nomenclature rules for naming $(\text{NPCl}_2)_3$ results in: 1,1,3,3,5,5-hexachloro-2,4,6,1 λ^5 ,3 λ^5 ,5 λ^5 -triazatriphosphorine, the compounds in this thesis are described by their formulae or in some cases trivial names will be used [75,76].

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