EurJIC European Journal of Inorganic Chemistry

ChemPubSoc Europe

FULL PAPER

DOI:10.1002/ejic.201301012

Synthesis and Oligomerization of Cyclodiphosph(V)azene Adducts

CLUSTER ISSUE

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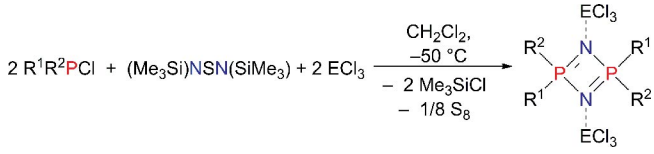
Keywords: Adducts / Bonding / Cyclodiphosphazenes / Phosphorus / Polymerization / Polyphosphazenes / Structure elucidation

The reaction of R^1R^2PCl (R^1 = Me, Ph; R^2 = Ph, *o*Tol) with *N*,*N*′-bis(trimethylsilyl)sulfur diimide in the presence of $GaCl_3$ yields Lewis acid/base adducts of the corresponding cyclodiphosph(V)azenes: $[MePhPN]_2{\cdot}(GaCl_3)_2$, $[Me(dmp)PN]_2{\cdot}(GaCl_3)_2$ (dmp = 2,6-dimethylphenyl), and $[Ph(oTol)PN]_2{\cdot}(GaCl_3)_2$. The same synthetic protocol was applied for the model compound Ph_2AsCl. All isolated products were characterized spectroscopically and by single-crystal X-ray diffraction studies. Their ability to form oligomers/polymers induced by abstraction of the Lewis acid was investigated with the model compounds $[MePhPN]_2{\cdot}(GaCl_3)_2$ and $[Ph_2PN]_2{\cdot}(GaCl_3)_2$.

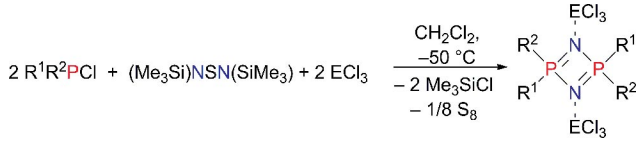
Introduction

Polyphosphazene derivatives are the largest class of inorganic macromolecules, and their importance in industrial applications is defined by their broad range of properties.[1,2] The preparation of the most significant starting material for synthesizing these macromolecules dates back to 1834, when Liebig and Wöhler isolated the cyclic hexachlorotriphosphazene $(PNCl_2)_3$ from the reaction of phosphorus pentachloride and ammonium chloride.[3] Over the last five decades, myriads of cyclotriphosph(V)azenes, tetraphosph(V)azenes, and polyphosph(V)azenes were prepared,[4] but only a few members of the cyclodiphosph(V)azene class have been synthesized and fully characterized (Scheme 1).[5] The first cyclodiphosph(V)azene was reported by Bertrand, Majoral, and co-workers, who introduced the photolysis of phosphorus azides as a method to prepare the first "heterocyclobutadiene" in 1984.[5a] Only recently, Bertrand reported on the isolation of the monomer R_2PN, a formal nitridophosphane(V).[6]



Scheme 1. Structurally characterized cyclodiphosph(V)azenes. ter = 2,6-bis(2,4,6-trimethylphenyl)phenyl, Mes* = 2,4,6-tri-*tert*-butylphenyl, Cp* = pentamethylcyclopentadiene.[5a–5c]

Hitherto, three synthetic routes to cyclodiphosph(V)azenes are known, and all require azides as a reagent; the formation of the cyclodiphosph(V)azenes proceeds under release of molecular nitrogen.[4] Only a few years ago, a novel synthetic route to cyclodiphosph(V)azenes was reported by Schulz et al.[7] In a reaction of chlorophosphanes with *N*,*N*′-bis(trimethylsilyl)sulfur diimide, $Me_3Si–NSN–SiMe_3$, the elimination of Me_3SiCl and S_8 is triggered by Lewis acids such as $AlCl_3$ and $GaCl_3$, and the diadducts of the corresponding cyclodiphosph(V)azenes, $[Ph_2PN]_2{\cdot}(GaCl_3)_2$ (**1**), $[Ph_2PN]_2{\cdot}(AlCl_3)_2$, and $[PhClPN]_2{\cdot}(AlCl_3)_2$, were isolated and fully characterized (Scheme 2).



Scheme 2. Synthesis of adducts of cyclodiphosph(V)azenes. R^1 = R^2 = Ph, E = Ga, Al; R^1 = Ph, R^2 = Cl, E = Al;[7] R^1 = Me, R^2 = Ph or dmp, E = Ga; R^1 = Ph, R^2 = *o*Tol, E = Ga.

Herein we report on the synthesis and characterization of diadducts of cyclodiphosph(V)azenes $[MePhPN]_2{\cdot}(GaCl_3)_2$

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Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/ejic.201301012.

(**2**), [Me(dmp)PN]$_2$·($GaCl_3$)$_2$ (**3**), and [Ph(*o*Tol)PN]$_2$·($GaCl_3$)$_2$ (**4**) and polymerization attempts by utilizing [Ph_2PN]$_2$·($GaCl_3$)$_2$ (**1**) and [PhMePN]$_2$·($GaCl_3$)$_2$ (**2**) as model compounds.

Results and Discussion

Synthesis of Cyclodiphosphadiazene

Lewis acid catalyzed cyclization reactions have been intensively studied in phosphorus–nitrogen chemistry.[8] For instance, in the synthesis of triazadiphospholes, $(Me_3Si)_2N–P_2N_3$, $GaCl_3$ as a Lewis acid triggers the elimination of Me_3SiCl from *N*,*N*′,*N*′-dichloro[tris(trimethylsilyl)hydrazino]phosphane prior to the cyclization step.[8a] A similar concept of Lewis acid catalysis was used for the preparation of cyclodiphosph(V)azene adducts.

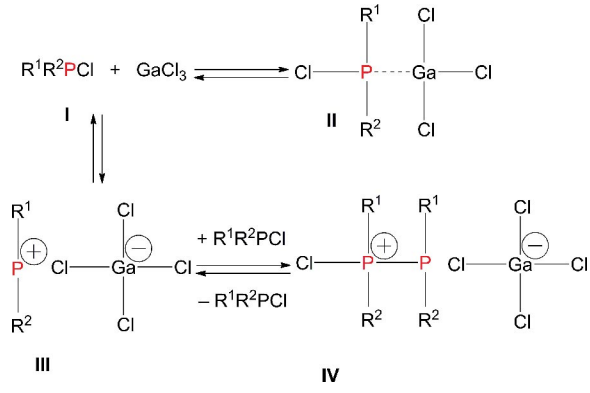
Starting at a low temperature of –50 °C, a stirred solution of $GaCl_3$ in dichloromethane was slowly combined with a solution of chlorophosphane, R^1R^2PCl, in dichloromethane and then with *N*,*N*′-bis(trimethylsilyl)sulfur diimide, $Me_3Si–NSN–SiMe_3$ (Scheme 2). The obtained solution was slowly warmed to ambient temperature over a period of 4 h. At a temperature of about –10 °C, a white precipitate was observed, which was identified as the corresponding cyclodiphosph(V)azene adduct and isolated in moderate yield. By increasing the steric demand of the chlorophosphanes, we observed a slightly higher yield in the synthesis of the cyclodiphosph(V)azene adducts. Chlorophosphanes with oversized bulky groups gave no reaction with the sulfur diimide, as stable Lewis acid/base adducts were formed (e.g., tBu_2PCl·$GaCl_3$, see below).

The main product in the reaction of MePhPCl[9] and $Me_3Si–NSN–SiMe_3$ in the presence of $GaCl_3$ was the *trans* isomer of cyclodiphosphadiazene, *trans*-**2**, which was detected by ^{31}P NMR spectroscopy as a singlet at $\delta(^{31}P)$ = 84.8 ppm (Scheme 2). The *cis* isomer (*cis*-**2**) was also generated in small amounts (ca. 2%), as shown by a singlet resonance at $\delta(^{31}P)$ = 85.8 ppm. Compound **2** (98% *trans*, 2% *cis* isomer) has a decomposition temperature of 314 °C [cf. ($Ph_2PN)_2(GaCl_3)_2$, T_{dec} = 370 °C].[7] The reaction of chloro(2,6-dimethylphenyl)methylphosphane yielded only *cis*-**3**. Only one singlet was detected at $\delta(^{31}P)$ = 88.9 ppm. Compound **3** has a decomposition temperature of 325 °C, which is slightly higher than that of **2**. Compound **4** with *o*Tol/Ph groups was detected by ^{31}P NMR spectroscopy at $\delta(^{31}P)$ = 74.9 ppm as the *cis* isomer, and it has a decomposition temperature of 365 °C.

Mechanistic Study of Cyclodiphosphadiazene Formation

The reaction mechanism is not completely understood, but in the absence of $GaCl_3$, no reaction of chlorophosphanes with *N*,*N*′-bis(trimethylsilyl)sulfur diimide occurs at low and ambient temperatures.

Presumably, in the first step of the reaction, $GaCl_3$ reacts with chlorophosphane (**I**) to develop an equilibrium between the coordination complex $R^1R^2(Cl)P$·$GaCl_3$ (**II**) and the diphosphorus cation $[R^1R^2(Cl)P–PR^1R^2]^+$ (**IV**, Scheme 3). Burford et al. investigated the reaction of chloro(dialkyl/diaryl)phosphanes with gallium trichloride in a systematic NMR spectroscopy study and described the presence of different species related by equilibrium in solution depending on the substituent at the phosphorus atom and the reaction stoichiometry.[10] In this context, further investigations according to the herein deployed chlorophosphanes were made.



Scheme 3. Equilibrium in solution of the reaction of R^1R^2PCl and $GaCl_3$.

The reaction with the sulfur diimide only occurs if the equilibrium lies on the side of the $[R^1R^2(Cl)P–PR^1R^2]^+$ cation (**IV**). It can be assumed that the cationic phosphorus atom attacks a nitrogen atom of *N*,*N*′-bis(trimethylsilyl)-sulfur diimide, and according to the overall reaction, sulfur and Me_3SiCl are eliminated.[11] The Lewis acid adducts of phosphanes **II** are not able to react with the sulfur diimide.

The equilibrium of an equimolar reaction of MePhPCl and $GaCl_3$ in solution observed by ^{31}P NMR spectroscopy is shown in Figure 1. For the phosphanylphosphonium cation $[MePh(Cl)P–PMePh]^+$, a total of four doublets results owing to the presence of two conformational isomers in a ratio of 4:5; the resonances for conformer 1 have chemical shifts of $\delta(^{31}P)$ = 85.6 and –16.1 ppm ($^1J_{P,P}$ = 355 Hz), and the resonances for conformer 2 have chemical shifts of $\delta(^{31}P)$ = 84.2 and –20.9 ppm ($^1J_{P,P}$ = 355 Hz) {cf. $[Ph_2(Cl)P–PPh_2]^+$: δ = 73 and 1 ppm, $^1J_{P,P}$ = 393 Hz; $[Me_2(Cl)P–PMe_2]^+$: δ = 96 and –28 ppm, $^1J_{P,P}$ = 311 Hz}.[10] The singlet resonance of the observed MePhPCl·$GaCl_3$ donor–acceptor complex is observed at $\delta(^{31}P)$ = 45.6 ppm, which is the typical range for such complexes [cf. $Ph_2(Cl)P$·$GaCl_3$: δ = 41 ppm; $Me_2(Cl)P$·$GaCl_3$: δ = 57 ppm].[10] In addition, a very small, very broad resonance is observed at δ = 55 ppm, which could not be assigned.

The monophosphonium cationic species $[MePhP]^+$ (**III**) and uncoordinated MePhPCl (**I**) are not observed. The ratio of observed species **IV**/**II** according to inserted MePhPCl is ca. 8:1. By increasing the steric bulk of the substituent on the chlorophosphane, the formation of $GaCl_3$ complex **II** was favored. Substitution of the phenyl group by a 2,6-dimethylphenyl group (dmp) decreased the ratio of the phosphanylphosphonium cation [Me(dmp)(Cl)

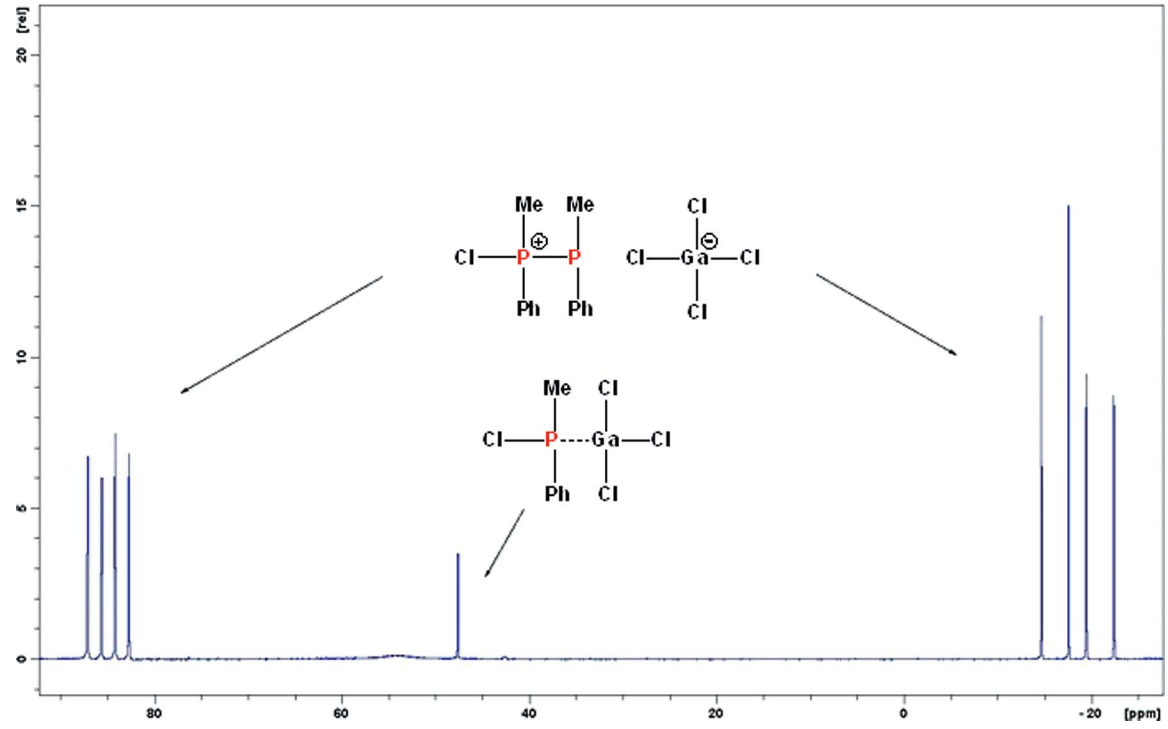


Figure 1. ^{31}P NMR spectrum of an equimolar reaction of MePhPCl with $GaCl_3$.

P–PMe(dmp)]$^+$ to the coordination complex Me(dmp)(Cl)P·$GaCl_3$ according to the inserted chlorophosphane to nearly 2:1. As an additional effect, one isomer of the diphosphorus cation was promoted with a new ratio of 2:1. In the case of the *o*Tol/Ph compound, the cation/adduct ratio decreased to below 1:1. The formation of the phosphane–gallium trichloride adduct was clearly favored, and the ratio of the isomers is nearly equal. By using chlorophosphanes with sterically more demanding substituents such as the *tert*-butyl group, the equilibrium of an equimolar reaction with $GaCl_3$ lies far to the chlorophosphane–gallium trichloride adduct. In this case, only one broad singlet with a chemical shift of δ = 102.4 ppm is observed for tBu$_2$PCl·($GaCl_3$) (**5**; Table 1; Supporting Information, Figure S1).

Table 1. ^{31}P NMR spectroscopic data and assignments for reaction mixtures R^1R^2(Cl)P and $GaCl_3$ (1:1).

R^1/R^2	δ [ppm] (J [Hz]) $[R^1R^2(Cl)P–R^1R^2P]^+$	δ [ppm] (rel. int.[a] [%]) $R^1R^2(Cl)P–GaCl_3$
Me/Me[b]	96 (311), –28 (311)	57 (< 5)
Ph/Ph[b]	73 (393), 1 (391)	41 (< 10)
Me/Ph[c]	85.6 (355), –16.1 (355)	45.6 (ca. 5)
	84.2 (355), –20.9 (355)	
Me/dmp[c]	83.0 (395), –9.2 (395)	34.3 (ca. 10)
	80.4 (405), –10.9 (405)	
*o*Tol/Ph[c]	73.6 (397), –0.8 (397)	38.5 (ca. 25)
	72.0 (404), –7.4(404)	
*t*Bu/*t*Bu	–	102.4 (100)

[a] Relative integration with respect to the principal signal given. [b] No fractional digits available, taken from ref.[10] [c] Two isomers of phosphanylphosphonium cation were observed.

In an equimolar reaction of gallium trichloride with the chlorophosphane, free Lewis acid is always present in solution if the equilibrium is on side of phosphanylphosphonium cation **IV**. In this case, the formation of an additional adduct after the addition of *N*,*N*′-bis(trimethylsilyl)sulfur diimide is implicated.[12] This leads to stretching of the Si–N and S–N bonds of the $GaCl_3$-coordinated N atom, which probably favors a reaction with the diphosphorus cation and the formation of the cyclodiphosph(V)azene adduct.

Reaction of Ph_2AsCl with Bis(trimethylsilyl)sulfur Diimide

In concurrent investigations, the synthesis of an arsenic-analogous cyclodiarsa(V)azene adduct was attempted in a reaction with Ph_2AsCl.[13] In contrast to Ph_2PCl, the arsenic compound was able to react with bis(trimethylsilyl)-sulfur diimide in the absence of gallium trichloride under the formation of bis(diphenylarsanyl)sulfur diimide (**6**).[14] Several attempts to obtain a defined reaction with the sulfur diimide and gallium trichloride always led to a yellow oil without any trace amount of a cyclodiars(V)azene adduct or any other defined product. However, it was possible to isolate small crystals during one reaction, which were identified by single-crystal X-ray diffraction to be Ph_2As–N=S=N–$SiMe_3$·$GaCl_3$ (**7**; Supporting Information, Figure S2). The formation of a cyclodiars(V)azene adduct was not observed, as no sulfur was eliminated in this case. Nevertheless, characterization of **7** could give further insight into the reaction mechanism of the cyclodiphosph(V)-azenes, as the analogous phosphorus compound could be expected as an intermediate.

Structure Elucidation

Single-crystal X-ray structure analysis was carried out for cyclodiphosph(V)azene adducts *trans*-**2**, *cis*-**2**, **3**, and **4**. Crystallographic details are listed in Tables 3 and 4. Furthermore, the structures of **5** and **7** are discussed briefly. For $(Ph_2AsN)_2S$ (**6**), a new polymorph was found.[13,14b]

In general, the metrical parameters of the P_2N_2 ring system of all considered cyclodiphosph(V)azene adducts are similar to those of $[Ph_2PN]_2{\cdot}(GaCl_3)_2$ (**1**, Table 2).[7] The P_2N_2 ring is distorted with two slightly different P–N bond lengths between 1.65 and 1.67 Å, which is substantially shorter than the sum of the covalent radii for a P–N bond [Σr_{cov}(N–P) = 1.8 Å, Σr_{cov}(N=P) = 1.6 Å],[15] which indicates partial double-bond character. The Ga–N bond length of 1.92–1.94 Å is in the typical range found for other $GaCl_3$ adducts [cf. 1.978(3) Å in triazadiphosphole and 1.965(2) Å in $(Me_3Si–N)_2S{\cdot}GaCl_3$].[8a,12,16]

Table 2. Selected bond lengths [Å] and angles [°] for **1**, *trans*-**2**, *cis*-**2**, **3**, and **4**.

	1[7]	*trans*-**2**	*cis*-**2**	**3**·CH_2Cl_2	**4**
P1–N1	1.680(4)	1.663(2)	1.673(3)	1.666(2)	1.672(2)
P1–N2	1.671(3)	1.667(2)	1.654(3)	1.678(2)	1.673(2)
P2–N1	1.680(4)	1.663(2)	1.661(3)	1.679(2)	1.672(2)
P2–N2	1.671(3)	1.667(2)	1.667(4)	1.668(2)	1.673(2)
Ga1–N1	1.937(4)	1.927(2)	1.924(3)	1.934(2)	1.945(2)
Ga2–N2	1.937(4)	1.927(2)	1.923(3)	1.934(2)	1.945(2)
N2–P1–N1	88.7(2)	88.3(1)	89.2(1)	88.67(8)	88.37(9)
N2–P2–N1	88.7(2)	88.3(1)	89.10(1)	88.58(8)	88.37(9)
P2–N1–P1	91.3(2)	91.7(1)	90.6(1)	91.30(8)	91.54(9)
P2–N2–P1	91.3(2)	91.7(1)	91.1(1)	91.28(8)	91.54(9)
∠NPPN	180	180	178.9(2)	175.5(1)	175.3(1)

Adduct *trans*-**2** crystallizes from dichloromethane as colorless crystal blocks without solvent molecules in the triclinic $P\bar{1}$ space group with two units per cell. As depicted in Figure 2, the P_2N_2 ring is planar (∠NPPN = 180°), and a center of inversion is found in the centroid of the P_2N_2 ring. Thus, a staggered conformation is found for both $GaCl_3$ moieties. The $GaCl_3$ groups are not completely in plane with the PN ring (∠N1^i–P1–N1–Ga1 = 175.3°), and in each case, one chlorine atom of the $GaCl_3$ moiety interacts intramolecularly with a hydrogen atom of an adjacent methyl group. The distance of the intermolecular Cl···H contact is about 2.87 Å.

Although *cis*-**2** was isolated in very small amounts (< 3%), it was possible to obtain single crystals for X-ray structure analysis. Compound *cis*-**2** crystallizes as colorless thin plates in the orthorhombic *Pbca* space group with four units per cell (Figure 3). The P_2N_2 ring is nearly planar [∠NPPN = 178.95(2)°]. The $GaCl_3$ moieties are found in an ecliptic conformation and are nearly in plane with the ring system (∠N2–P1–N1–Ga1 = 178.71°). In contrast to *trans*-**2**, no significant intermolecular Cl···H interactions are found, but intramolecular Cl···H interactions do exist. Cl1 is in contact with a hydrogen atom of a methyl group C1 ($d_{Cl\cdots H}$ = 2.87 Å), and Cl3 interacts with an aryl hydrogen atom of one phenyl group ($d_{Cl\cdots H}$ = 2.75 Å). Owing to this interaction, the phenyl groups are more strongly twisted towards the $GaCl_3$ moieties than they are in *trans*-**2**.

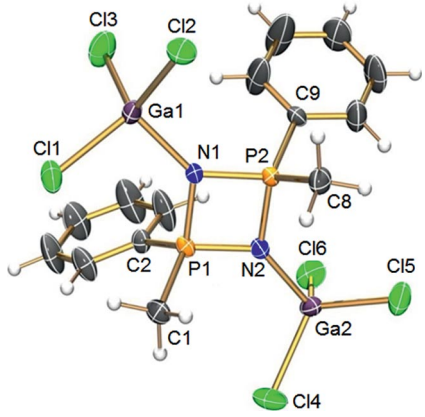


Figure 3. ORTEP drawing of the molecular structure of *cis*-**2** in the crystal. Thermal ellipsoids with 50% probability at 173 K.

Compound **3** crystallizes in the monoclinic $P2_1/c$ space group with four units per cell and a CH_2Cl_2 solvent molecule in the asymmetric unit (Figure 4). As a result of the sterically demanding aryl groups, the P_2N_2 ring loses its planarity (∠NPPN = 175.47°), and the $GaCl_3$ moieties are pushed out of the P_2N_2 plane (∠N1–P1–N2–Ga2 =

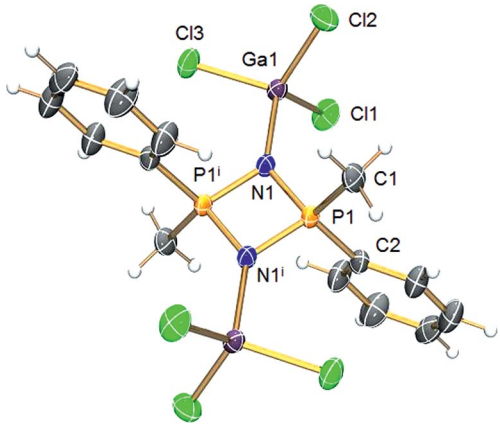


Figure 2. ORTEP drawing of the molecular structure of *trans*-**2** in the crystal. Thermal ellipsoids with 50% probability at 173 K.

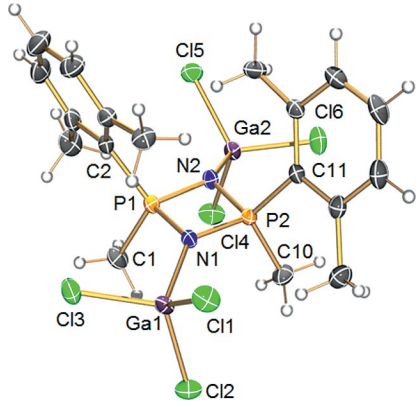


Figure 4. ORTEP drawing of the molecular structure of **3** in the crystal. Thermal ellipsoids with 50% probability at 173 K.

160.16°). Intermolecular and intramolecular Cl···H interactions can be observed. The methyl group attached to the phosphorus atom has a distance of 2.87 Å to a chlorine atom of an adjacent molecule. The Cl6 atom shows some intramolecular Cl···H interaction with the aryl methyl groups with distances of about 2.86 Å.

Diaryl compound **4** crystallizes in the tetragonal $P42_1c$ space group with four units per cell and one half of a CH_2Cl_2 solvent molecule in the asymmetric unit (Figure 5). The P_2N_2 ring is slightly distorted from planarity (∠NPPN = 175.47°). The $GaCl_3$ moieties are found in a staggered conformation and are nearly in plane with the ring system (∠N1^i–P1–N1–Ga1 = 177.25°). Two intermolecular Cl···H interactions of the $GaCl_3$ moieties with the hydrogen atoms in the *para* position to the *o*-toluene group of adjacent molecules with distances of about 2.76 Å are observed.

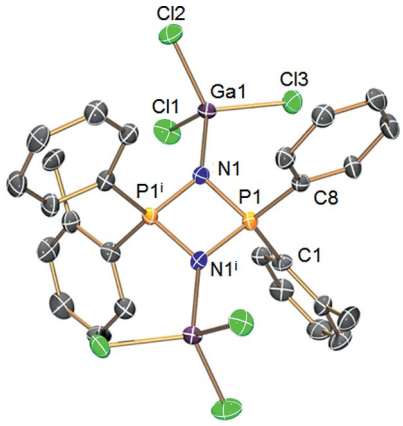


Figure 5. ORTEP drawing of the molecular structure of **4** in the crystal. Thermal ellipsoids with 50% probability at 173 K (hydrogen atoms omitted for clarity).

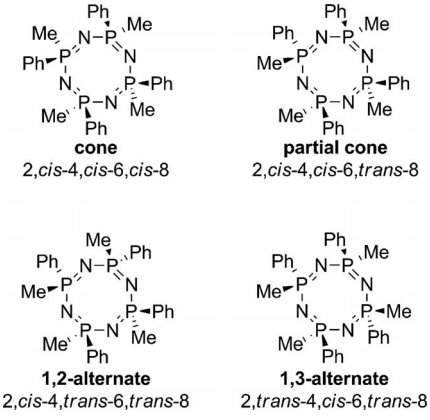
Attempted Ring-Opening Polymerization

There are three synthetic strategies to prepare polyorganophosphazenes (POPs):[1] (1) Preparation of polydichlorophosphazene, $(NPCl_2)_n$, a polymeric intermediate from which the large majority of POPs were prepared by nucleophilic substitution of the highly reactive chlorine atoms with carefully selected organic substituents. (2) Use of polycondensation processes of substituted phosphoranimines to obtain already substituted polyorganophosphazenes. (3) Utilization of ring-opening polymerization (ROP) processes of completely or partially substituted cyclophosphazenes to obtain POPs having predictable chemical structures. In 2006, the group of Manners found a new high-yielding synthetic route to high-molecular-weight poly(alkyl/aryl)phosphazenes $[RPhPN]_n$ (R = Me, Ph) by employing phosphites $(RO)_3P$ at ambient temperature.[1a,17]

In the synthesis of cyclodiphosph(V)azene diadducts, $GaCl_3$ as the Lewis acid has two assignments: (1) to trigger the elimination of Me_3SiCl and (2) to help in the kinetic stabilization of the dimeric form of the cyclophosph(V)azene. Early calculations by Ahlrichs and Schiffer indicated that the dimer is by far the most stable compound of all the possible noncyclic monomers.[18] Whereas, in general, the formation of tri- and tetramers appears to be thermodynamically favored, sterically overcrowded substituents force dimerization. The surprising stability of cyclodiphosph(V)azenes was attributed to the high thermodynamic energy of the monomer, which prevents dissociation, and to steric factors, which hinder polymerization.

In the case of $(MePhPN)_2{\cdot}(GaCl_3)_2$, the steric demand of the methyl and phenyl groups is considerably smaller than that of the isopropylamine, supermesityl, and terphenyl groups that were used for stabilization in the cyclodiphosph(V)azenes synthesized by Bertrand and Majoral et al., Wehmschulte et al., and Niecke et al. (Scheme 1).[5] However, the ring dimer in, for example, $(MePhPN)_2{\cdot}(GaCl_3)_2$, is additionally stabilized by the coordination of the $GaCl_3$ Lewis acid. In the interest of our research, we investigated the behavior of the $(MePhPN)_2{\cdot}(GaCl_3)_2$ (**2**) diadduct towards the abstraction of $GaCl_3$ by using Lewis bases to answer the question if it was possible to obtain a soluble polymer from Ph/Me-substituted ring dimers by ROP. For comparison, $(Ph_2PN)_2{\cdot}(GaCl_3)_2$ (**1**) was used as a model compound.

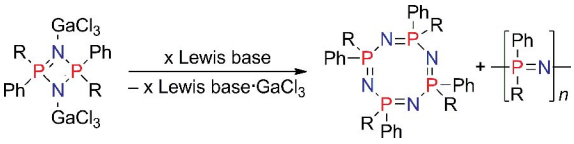
The reaction of $(MePhPN)_2{\cdot}(GaCl_3)_2$ with Lewis bases [e.g., DMAP = 4-(dimethylamino)pyridine, nBu$_3$P, Et$_3$N] was finished within seconds. The use of 2 equiv. of DMAP resulted in quantitative formation of the cyclic $(MePhPN)_4$ tetramer, as observed by ^{31}P NMR spectroscopy (δ = 10.8 and 10.4 ppm) independent of the reaction conditions. As shown in Scheme 4, four different structural isomers are possible (Scheme 4).



Scheme 4. Isomers of cyclotetraphosph(V)azenes.

On the basis of the fact that the cyclic Me/Ph-substituted dimer adduct basically has a *trans* conformation, the formation of the 1,2-alternated and 1,3-alternated cyclic tetramer was not unexpected. According to ^{31}P NMR spectroscopy, the formation of the 1,3-alternated isomer was slightly preferred. Any formation of the cone or partial cone isomers was not verifiable (Scheme 5).

Wisian-Neilson et al. reported first about the formation and characterization of all four diastereoisomers of methyl(phenyl)tetracyclophosphazene,[19] but for the isolation of each of the four structural isomers, an extensive isolation route was necessary. Starting with 20.0 g of pure *trans*-



Scheme 5. General reaction of cyclodiphosph(V)azenes with Lewis bases depending on R = Me, Ph.

[Me(Ph)PN]$_3$ heated at 250 °C for 6 d, a 2:1 ratio of trimers to tetramers was obtained. The isolation of each compound required several column chromatography steps, and by exploiting the different solubilities of the isomers, all of them were obtained in very moderate yields.

By using just 1 equiv. of Lewis base (DMAP or nBu$_3$P), another species in addition to the starting material and the cyclic tetramer was observed. An interpretation of the ^{31}P NMR spectrum was not clearly definable, but a tentative assignment of the linear tetrameric compound by four (DMAP-stabilized species) and five (nBu$_3$P-stabilized species) new ^{31}P NMR signals was possible. A second equivalent of Lewis base always led to the quantitative formation of the cyclic tetramer.

More interesting results were obtained from the reactions of the model compound, (Ph$_2$PN)$_2$·(GaCl$_3$)$_2$ (**1**), with nBu$_3$P or DMAP as the Lewis base. By abstracting GaCl$_3$ with 2 equiv. of nBu$_3$P, the cyclic tetramer (δ = 6.4 ppm) and another species were detected by ^{31}P NMR spectroscopy. This other species was identified as the linear tetramer with a GaCl$_3$ (Lewis acid) molecule and an nBu$_3$P (Lewis base) molecule at each side. A pattern of five resonances with a triplet at δ = 1.9 ppm ($^2J_{P,P}$ = 7.9 Hz), a doublet of triplets at δ = 9.6 ppm ($^2J_{P,P}$ = 7.9 Hz, $^3J_{P,P}$ = 19.0 Hz), a doublet at δ = 17.1 ppm ($^2J_{P,P}$ = 7.9 Hz), a doublet of doublets at δ = 17.2 ppm ($^1J_{P,P}$ = 15.7 Hz, $^2J_{P,P}$ = 19.0 Hz), and another doublet of duplets at δ = 37.6 ppm ($^1J_{P,P}$ = 15.7, $^3J_{P,P}$ = 19.0 Hz) appears.

In the reaction of (Ph$_2$PN)$_2$·(GaCl$_3$)$_2$ with 2 equiv. of DMAP, the formation of several species was observed by ^{31}P NMR spectroscopy. A singlet with a chemical shift of δ = 6.3 ppm is related to the cyclic tetramer.[20] Furthermore, the linear dimer, tetramer, and hexamer are detectable (Figure 6).

The linear dimer exhibits two doublets at δ = 28.3 and 25.5 ppm with $^2J_{P,P}$ = 9.7 Hz. Another pattern with four resonances fits to the linear tetrameric species: two doublets at δ = 28.6 ($^2J_{P,P}$ = 9.4 Hz) and 24.7 ppm ($^2J_{P,P}$ = 8.7 Hz) for the terminal phosphorus atom and two doublets of doublets for the interior phosphorus atom at δ = 5.0 ($^2J_{P,P}$ = 6.6 Hz, $^2J_{P,P}$ = 9.4 Hz) and 1.6 ppm ($^2J_{P,P}$ = 6.6 Hz, $^2J_{P,P}$ = 8.7 Hz). In addition, the ^{31}P NMR spectrum exhibited six resonances for the linear hexamer appearing at δ = 26.1 ($^2J_{P,P}$ = 11.7 Hz) and 23.9 ppm ($^2J_{P,P}$ = 9.4 Hz) for the terminal phosphorus atom. For their adjacent phosphorus atom, two doublets of doublets appear at δ = 2.3 ($^2J_{P,P}$ = 6.6 Hz, $^2J_{P,P}$ = 11.7 Hz) and 1.0 ppm ($^2J_{P,P}$ = 5.7 Hz, $^2J_{P,P}$ = 9.4 Hz). The two resonances for the interior phosphorus atoms are given as another doublet of doublets at δ = –2.5 ($^2J_{P,P}$ = 6.6 Hz, $^2J_{P,P}$ = 10.9 Hz) and –3.0 ppm ($^2J_{P,P}$ = 5.7 Hz, $^2J_{P,P}$ = 10.9 Hz). The occurrence of the linear dimer, tetramer, and hexamer species besides the cyclic tetramer was additionally confirmed by ESI mass spectrometry (Figure 7). Furthermore, the linear octamer was detected at m/z = 1630.42 (exact mass 1629.43), which was not verifiable by NMR spectroscopy. Notably, owing to the ESI process, DMAP and GaCl$_3$ were replaced by Cl and NH$_3$ groups.

In general, the formation of the Ph/Me- and Ph/Ph-substituted polymeric species was not possible by starting with cyclodiphosphazene diadducts. This may be a consequence of two factors: (1) Owing to the poor solubility of the cyclodiphosphazene diadducts in nearly all of the solvents, the abstraction of the GaCl$_3$ Lewis acid is rather slow. Therefore, the concentration of the uncoordinated cyclodiphosphazene may be too low to favor polymer formation. (2) During the polymerization reaction, the Lewis acid and the Lewis base may coordinate to the intermediates and hinder further polymerization. Additionally, the Ph/Me dimer favors the formation of cyclic tetramers if an equimolar amount or even an excess amount of the Lewis base is used. In all of our polymerization attempts for the Ph/Me-substi-

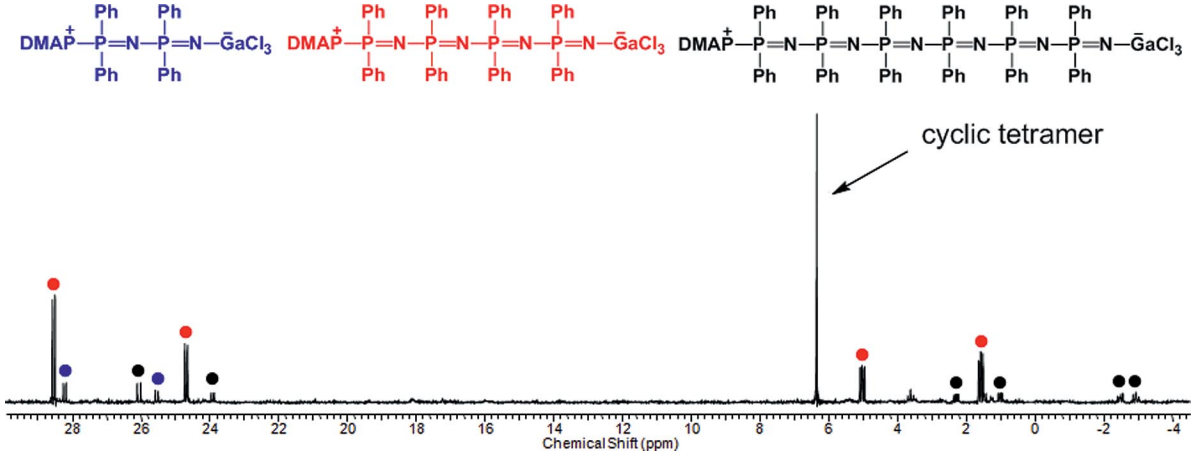


Figure 6. ^{31}P NMR spectrum of the reaction of (Ph$_2$PN)$_2$·(GaCl$_3$)$_2$ with DMAP (2 equiv.).

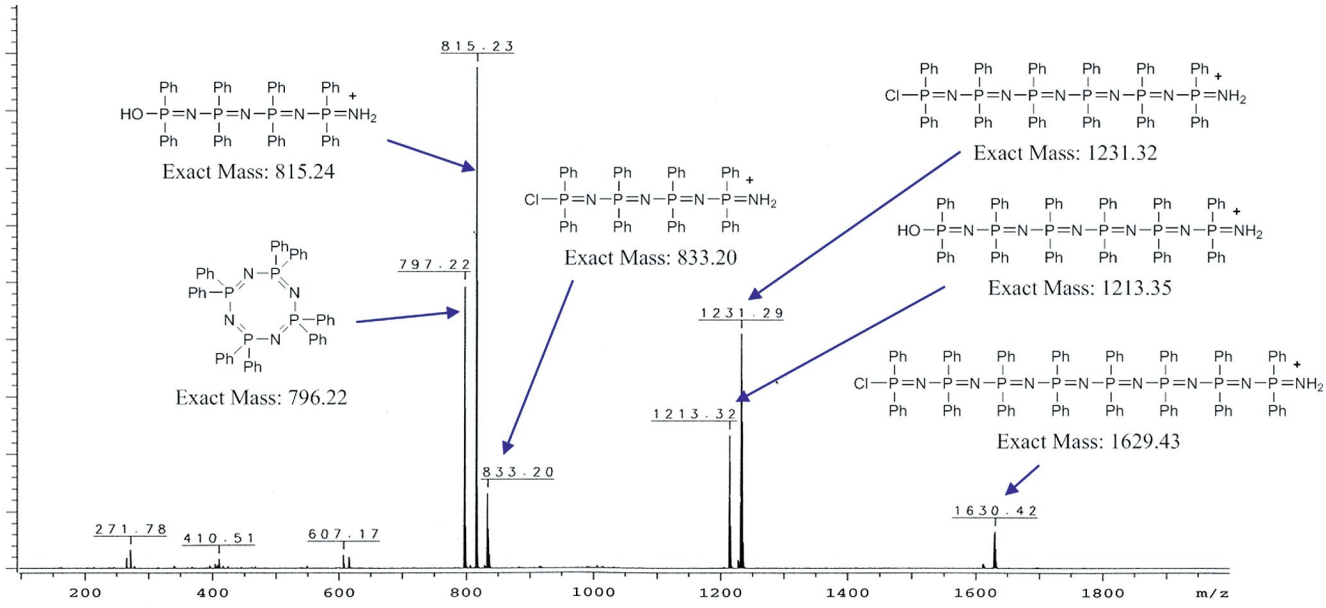


Figure 7. MS (ESI) of the end product of the reaction of $(Ph_2PN)_2{\cdot}(GaCl_3)_2$ with DMAP (2 equiv.).

tuted compound, no sign of polymer or chains longer than the tetramer were obtained. In contrast, the Ph/Ph dimer appears to form both linear and cyclic products independently from the amount of Lewis base used. The formation of linear species is favored, which is in contrast to the Ph/Me-substituted cyclic dimers, and at least the linear octamer is formed. Unfortunately, the high-molecular-weight Ph/Ph-substituted polymer is insoluble and difficult to characterize, but no material consistent with its formation was noted during the attempted polymerization reactions.

Conclusions

We presented new derivatives of cyclodiphosph(V)azenes from the reaction of chlorophosphanes with *N*,*N*′-bis(trimethylsilyl)sulfur diimide, $Me_3Si–NSN–SiMe_3$, triggered by the action of $GaCl_3$. The steric influence of the substituent at the phosphane was discussed as well as the necessity for the formation of an $[R^1R^2(Cl)P–PR^1R^2]^+$ cation for this type of reaction. The heavier Ph_2AsCl congener reacted with $Me_3Si–NSN–SiMe_3$ in the presence of $GaCl_3$ to give $Ph_2As–N{=}S{=}N–SiMe_3{\cdot}GaCl_3$. In contrast to the phosphorus species, the elimination of S_8 was not observed. Furthermore, Ph/Me- and Ph/Ph-substituted compounds **1** and **2** were investigated with respect to their ring-opening polymerization. This led mainly to the cyclic tetramer (for **1**) and at most to the linear octamer species (for **2**). Studies of the polymerization behavior of more soluble analogues of Lewis acid stabilized cyclodiphosph(V)azenes would be a worthwhile subject for future work.

Experimental Section

General Information: All manipulations were carried out under oxygen- and moisture-free conditions under argon by using standard Schlenk or dry-box techniques. Dichloromethane was purified according to a literature procedure, dried with P_4O_{10}, and freshly distilled prior to use.[21] *N*,*N*′-Bis(trimethylsilyl)sulfur diimide was prepared according to a modified literature procedure.[22] MePhPCl, (dmp)PhPCl, and *o*TolPhPCl were prepared according to literature procedures.[23] tBu_2PCl (99%, Fluka) was freshly distilled prior to use. $GaCl_3$ (99.99%, Sigma–Aldrich) was used as received. Ph_2AsCl was prepared according to a literature procedure.[24] Information about the attempted synthesis of cyclodiars(V)azene adducts and the polymerization attempts can be found in the Supporting Information. $^{31}P\{^1H\}$, $^{13}C\{^1H\}$, ^{13}C DEPT, and ^1H NMR spectra were obtained with Bruker Avance 250, 300, and 500 or JEOL Lambda 300 and Eclipse 300 spectrometers and were referenced internally to the deuterated solvent (^{13}C, CD_2Cl_2: $\delta_{reference}$ = 54 ppm) or to protic impurities in the deuterated solvent (^1H, $CDHCl_2$: $\delta_{reference}$ = 5.31 ppm). The IR spectra were recorded with a Nicolet 380 FTIR with a Smart Orbit ATR device. Raman spectra were recorded with a Bruker Vertex 70 FTIR with RAM II FT-Raman module equipped with an Nd:YAG laser (1064 nm) or with a Kaiser Optical Systems RXN1-785 nm. ESI mass spectra were recorded with a Bruker Daltonics Apex IV Fourier transform ion cyclotron resonance mass spectrometer, and EI and CI mass spectrometry were carried out with a VG Analytical AutoSpec mass spectrometer or a Finnigan MAT 95-XP from Thermo Electron. CHN analyses were performed with an Analysator Flash EA 1112 from Thermo Quest or a C/H/N/S-Mikronalysator TruSpec-932 from Leco. Melting points were recorded with an EZ-Melt, Stanford Research Systems, with a heating rate of 20 °C min^{-1} (clearing-points are reported). Differential scanning calorimetry (DSC) was performed with a DSC 823e from Mettler-Toledo with a heating rate of 5 °C min^{-1}.

X-ray Structure Determination: X-ray-quality crystals of all compounds were selected in Kel-F-oil (Riedel–de Haën) or Fomblin YR-1800 perfluoroether (Alfa Aesar) at ambient temperature. The samples were cooled to 173(2) K during measurement. The data was collected with a Bruker Kappa Apex-II CCD diffractometer by using graphite-monochromated Mo-K_α radiation (λ = 0.71073). The structures were solved by direct methods (SHELXS-97)[25] and refined by full-matrix least-squares procedures (SHELXL-97).[26]

Table 3. Crystallographic details of **1**, *trans*-**2**, *cis*-**2**, **3**, and **4**.

	cis-**2**	*trans*-**2**	**3**·CH_2Cl_2	**4**·0.5CH_2Cl_2
Empirical formula	$C_{14}H_{16}Cl_6Ga_2N_2P_2$	$C_{14}H_{16}Cl_6Ga_2N_2P_2$	$C_{18}H_{24}Cl_6Ga_2N_2P_2$·$CH_2Cl_2$	$C_{26}H_{24}Cl_6Ga_2N_2P_2$·0.5$CH_2Cl_2$
Formula mass	626.37	626.37	767.40	821.02
Color	colorless	colorless	colorless	colorless
Crystal system	triclinic	orthorhombic	monoclinic	tetragonal
Space group	$P\bar{1}$	*Pbca*	$P2_1/c$	$P\bar{4}2_1c$
a [Å]	8.758(5)	14.8995(5)	11.433(5)	13.2711(2)
b [Å]	9.837(6)	9.2766(3)	12.642(6)	13.2711(2)
c [Å]	14.936(9)	16.6902(6)	20.859(8)	18.2860(5)
α [°]	80.659(1)	90	90	90
β [°]	75.957(1)	90	98.90(1)	90
γ [°]	72.74(2)	90	90	90
V [Å^3]	1186.5(1)	2306.9(1)	2979 (2)	3220.57(1)
Z	2	4	4	4
$\rho_{calcd.}$·[g cm^{-3}]	1.753	1.804	1.711	1.693
μ [mm^{-1}]	3.084	3.173	2.648	2.375
λ(Mo-K_α) [Å]	0.71073	0.71073	0.71073	0.71073
T [K]	173(2)	173(2)	173(2)	173(2)
Measured reflections	19049	12987	23298	16744
Independent reflections	5406	3056	8634	3888
Reflections with $I > 2\sigma(I)$	3340	2362	6997	3444
$R_{int.}$	0.0492	0.0331	0.0288	0.0391
F(000)	616	1232	1528	1636
R_1 {$R[F^2 > 2\sigma(F^2)]$}	0.0374	0.0349	0.0285	0.0261
wR_2 (all data)	0.0707	0.0980	0.0702	0.0580
GooF	0.933	1.059	1.049	1.008
Parameters	237	120	314	185

Table 4. Crystallographic details of **5**, **6**, and **7**.

	5	**6**	**7**
Empirical formula	$C_8H_{18}Cl_4GaP$	$C_{24}H_{20}As_2N_2S$	$C_{15}H_{19}AsCl_3GaN_2SSi$
Formula mass	356.71	518.32	538.46
Color	colorless	yellow	yellow
Crystal system	monoclinic	monoclinic	triclinic
Space group	$P2_1/n$	*C*2/*c*	$P\bar{1}$
a [Å]	9.0310(4)	18.2635(6)	9.7832(5)
b [Å]	15.2834(8)	5.8395(2)	11.2660(6)
c [Å]	10.7635(5)	20.8645(6)	11.6349(6)
α [°]	90	90	68.767(3)
β [°]	90.589(2)	105.9440(1)	83.625(3)
γ [°]	90	90	66.190(3)
V [Å^3]	1485.55(1)	2139.59(1)	1092.65(1)
Z	4	4	2
$\rho_{calcd.}$·[g cm^{-3}]	1.595	1.609	1.637
μ [mm^{-1}]	2.646	3.234	3.280
λ(Mo-K_α) [Å]	0.71073	0.71073	0.71073
T [K]	173(2)	173(2)	173(2)
Measured reflections	17811	13595	26886
Independent reflections	4304	3822	7310
Reflections with $I > 2\sigma(I)$	4003	2990	4423
$R_{int.}$	0.0181	0.0278	0.0614
F(000)	720	1040	536
R_1 {$R[F^2 > 2\sigma(F^2)]$}	0.0188	0.0286	0.0406
wR_2 (F^2)	0.0472	0.0613	0.0788
GooF	1.049	1.031	0.991
Parameters	133	132	220

Semiempirical absorption corrections were applied (SADABS).[27] All non-hydrogen atoms were refined anisotropically; hydrogen atoms were included in the refinement at calculated positions by using a riding model (Tables 3 and 4). CCDC-955010 (for *cis*-**2**), -955009 (for *trans*-**2**), -955011 (for **3**·CH_2Cl_2), -955012 (for **4**·0.5CH_2Cl_2), -955012 (for **5**), -955013 (for **6**), and -955015 (for **7**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

General Synthesis of Cyclodiphosph(V)azenes Adducts: The corresponding chlorophosphane (2.0 mmol) was added slowly by syringe to a solution of $GaCl_3$ (2.0 mmol) in CH_2Cl_2 (10 mL) at –50 °C.

The resulting mixture was stirred at this temperature for 15 min, and then pure *N*,*N*′-bis(trimethylsilyl)sulfur diimide (1.0 mmol) was added dropwise. The resulting mixture was slowly warmed to ambient temperature over 4 h whilst stirring, and a white precipitate formed. The resulting suspension was concentrated and filtered, and the colorless precipitate was washed several times with small amounts of CH_2Cl_2. For further purification, the crude product was recrystallized from CH_2Cl_2.

$(MePhPN)_2(GaCl_3)_2$ (2): Yield: 0.16 mmol, 16%. M.p. 315 °C (dec.). $C_{14}H_{16}Cl_6Ga_2N_2P_2$ (626.40): calcd. C 26.84, H 2.57, N 4.47; found C 26.34, H 2.69, N 4.22. $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_2Cl_2, 25 °C): δ = 84.8 ppm. ^1H NMR (300 MHz, CD_2Cl_2, 25 °C): δ = 2.90 [d, $^2J(^1H\text{-}^{31}P)$ = 14.0 Hz, 6 H, CH_3], 7.81 (m, 4 H, *o*-H), 7.98 (t, *J* = 7.35 Hz, 2 H, *p*-H), 8.11 (m, 4 H, *m*-H) ppm. IR (ATR, 25 °C, 32 scans): $\tilde{\nu}$ = 3068 (w), 2991 (w), 2908 (m), 1810 (w), 1588 (m), 1552 (w), 1487 (w), 1438 (s), 1387 (w), 1339 (w), 1312 (m), 1298 (m), 1164 (w), 1120 (s), 1003 (vs), 908 (vs), 840 (s), 825 (s), 767 (m), 740 (vs), 730 (s), 680 (s), 573 (s) cm^{-1}. Raman (100 mW, 25 °C, 302 scans): $\tilde{\nu}$ = 3073 (4), 2998 (2), 2984 (5), 1586 (5), 1398 (1), 1190 (1), 1166 (1), 1119 (2), 1027 (2), 999 (10), 616 (2), 568 (2), 400 (2), 361 (5), 246 (2), 170 (2), 135 (2), 115 (4) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 46(15), 51(13), 57(12), 69(16), 71(17), 77(37) $[C_6H_5]^+$, 78(20), 91 (38), 109(12), 121(13), 122(32), 123(12), 124(15), 125(10), 136(14), 138(42), 139(51), 140(16),183(18), 199(19), 201(13), 215(95), 216(29), 260(10), 261(91), 262(16), 276(67) $[(MePhPN)_2 + 2\ H]^{2+}$, 277(55), 278(10), 291(12), 305(36), 319 (20), 320 (78), 321(17), 359(11) 379(48), 381(57), 383(12), 395(58), 396(13), 397(58), 398(10), 399(16), 415(72), 416(14), 417(100), 418(17), 419(41), 430(24), 432(30), 434(13), 459(15) 461(20). Crystals suitable for X-ray crystallographic analysis were obtained by cooling a saturated CH_2Cl_2 solution of **2** to –40 °C.

$[Me(dmp)PN]_2(GaCl_3)_2$ (3): Yield: 0.25 mmol, 25%. M.p. 326 °C (dec.). $C_{18}H_{24}Cl_6Ga_2N_2P_2$ (682.51): calcd. C 31.68, H 3.54, N 4.10; found C 31.48, H 3.68, N 3.39. $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_2Cl_2, 25 °C): δ = 88.9 ppm. ^1H NMR (300 MHz, CD_2Cl_2, 25 °C): δ = 2.94 [d, $^2J(^1H,^{31}P)$ = 13.3 Hz, 6 H, P-CH_3], 2.88 [s, 12 H, C_6H_3-(CH_3)$_2$], 7.58 (t, *J* = 7.86 Hz, 2 H, *p*-H), 7.60 (m, 4 H, *m*-H) ppm. IR (ATR, 25 °C, 32 scans): $\tilde{\nu}$ = 3068 (w), 3011 (w), 2992 (w), 2922 (w), 1588 (m), 1566 (w), 1454 (s), 1392 (m), 1377 (w), 1301 (m), 1251 (w), 1243 (w), 1173 (m), 1138 (m), 1060 (s), 1024 (m), 978 (vs), 909 (s), 898 (vs), 883 (vs), 817 (s), 787 (s), 779 (s), 737 (s), 709 (m) 578 (m), 534 (m) cm^{-1}. Raman (1500 mW, 25 °C, 500 scans): $\tilde{\nu}$ = 3060 (4), 3014 (3), 2993 (5), 2942 (7), 2924 (8), 1588 (6), 1458 (1), 1385 (3), 1244 (5), 1174 (1), 1068 (7), 785 (1), 532 (8), 400 (3), 364 (10), 209 (1), 147 (1), 125 (2) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 67(1), 257(1), 330(5) $[(dmpMePN)_2 + 2\ H^+]^{2+}$, 331(2), 361(2), 376(5), 377(3), 451(14), 452(3), 453(13), 454(3), 455(3), 469(26), 470(5), 471(34), 472(7), 473(13), 474(2), 475(1), 487(5), 488(2), 489(8), 490(2), 491(3), 515(72), 516(17), 517(100), 518(22), 519(31), 520(9), 521(6), 522(1), 893(1). Crystals suitable for X-ray crystallographic analysis were obtained by cooling a saturated CH_2Cl_2 solution of **3** to –40 °C.

$[Ph(o\text{Tol})PN]_2(GaCl_3)_2$ (4): Yield: 0.52 mmol, 52%. M.p. 365 °C (dec.). $C_{26}H_{24}Cl_6Ga_2N_2P_2$ (778.59): calcd. C 40.1, H 3.11, N 3.60; found C 39.62, H 3.33, N 3.43. $^{31}P\{^1H\}$ NMR (202.5 MHz, CD_2Cl_2, 25 °C): δ = 74.9 ppm. ^1H NMR (500 MHz, CD_2Cl_2, 25 °C): δ = 2.28 [s, 6 H, C_6H_4-(CH_3)], 7.47 [m, 2 H, C_6H_4-(CH_3)], 7.49 [m, 2 H, C_6H_4-(CH_3)], 7.72 (m, 4 H, *o*-H, C_6H_5), 7.81 (t, *J* = 7.6 Hz, 2 H, *p*-H, C_6H_5), 7.95 [t, *J* = 7.6 Hz, 2 H, *p*-H, C_6H_4-(CH_3)], 8.08 (m, 4 H, *m*-H, C_6H_5), 8.19 [m, 2 H, C_6H_4-(CH_3)] ppm. IR (ATR, 25 °C, 32 scans): $\tilde{\nu}$ = 3083 (w), 3059 (w), 2980 (w), 1951 (w), 1584 (w), 1564 (w), 1494 (w), 1446 (w), 1436 (m), 1417 (w), 1385 (w), 1312 (w), 1288 (w), 1278 (w), 1265 (w), 1199 (w), 1188 (w), 1167 (w), 1138 (m), 1107 (m), 1084 (m), 1051 (w), 1028 (w), 999 (w), 958 (s), 869 (vs), 836 (m), 810 (m), 761 (m), 746 (s), 739 (s), 714 (m), 703 (m), 681 (s), 669 (m), 628 (w), 612 (w), 569 (s) cm^{-1}. Raman: $\tilde{\nu}$ = (500 mW, 25 °C, 250 scans): 3061(4), 2928 (1), 1585(8), 1441 (1), 1393 (1), 1202 (1), 1167 (1), 1136 (1), 1113 (3), 1086 (1), 1051 (4), 1026 (2), 999 (6), 814 (1), 629 (2), 614 (1), 557 (1), 399 (1), 359 (6), 334 (1), 224 (4), 185 (1), 116 (6), 101 (10) cm^{-1}. Crystals suitable for X-ray crystallographic analysis were obtained by cooling a saturated CH_2Cl_2 solution of **4** to –40 °C.

Synthesis of $t\text{Bu}_2\text{PCl}(GaCl_3)$ (5): Bis(*tert*-butyl)chlorophosphane (0.180 g, 1.0 mmol) was added slowly by syringe to a solution of $GaCl_3$ (0.176 g, 1.0 mmol) in CH_2Cl_2 (10 mL) at –30 °C. The resulting mixture was stirred at this temperature for 15 min and warmed to ambient temperature. The solvent was removed, and the resulting colorless residue was dried in vacuo to yield **5** (0.350 g, 0.99 mmol, 99%). For further purification, the product was recrystallized from CH_2Cl_2. M.p. 176 °C (dec.). $C_8H_{18}Cl_4GaP$ (356.74): calcd. C 26.93, H 5.09; found C 26.66, H 5.27. $^{31}P\{^1H\}$ NMR (202.5 MHz, CD_2Cl_2, 25 °C): δ = 101.4 (br.) ppm. ^1H NMR (500 MHz, CD_2Cl_2, 25 °C): δ = 1.56 [d, $^3J(^1H,^{31}P)$ = 17.8 Hz, 18 H] ppm. ^{13}C NMR (125.7 MHz, CD_2Cl_2, 25 °C): δ = 27.9 [d, $^2J(^{13}C,^{31}P)$ = 4.5 Hz, 6 C, (CH_3)$_3$C], 41.6 [s, 2 C, (CH_3)$_3$*C*] ppm. IR (ATR, 25 °C, 32 scans): $\tilde{\nu}$ = 2967 (w), 2942 (w), 2897 (w), 2869 (w), 2395 (w), 1464 (s), 1398 (w), 1373 (s), 1169 (m), 1069 (w), 1023 (m), 940 (m), 935 (m), 898 (w), 798 (m), 717 (w), 621 (m), 592 (s), 560 (s) cm^{-1}. MS (CI+, isobutane): *m*/*z* (%) =183 (30), 181 (100) $[t\text{Bu}_2\text{PCl} + H]^+$, 145 (5) $[t\text{Bu}_2\text{P}]^+$. Crystals suitable for X-ray crystallographic analysis were obtained by cooling a saturated CH_2Cl_2 solution of **5** to –40 °C.

Supporting Information (see footnote on the first page of this article): Experimental details, structure elucidation, synthesis and reactions, and polymerization attempts.

Acknowledgments

Financial support by the Deutsche Forschungsgemeinschaft (DFG) (SCHU 1170/8-1) is gratefully acknowledged.

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Received: August 5, 2013
Published Online: September 19, 2013

