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Dichloro-cycloazatriphosphane — the missing link between N_2P_2 and P_4 ring systems in the systematic development of NP chemistry

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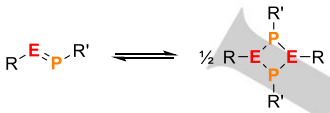
Dedicated to Prof. Dr. Evamarie Hey-Hawkins on the occasion of her 60th birthday

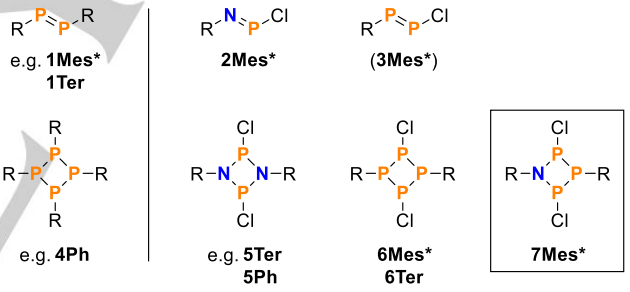
Abstract: A dichloro-cycloazatriphosphane that incorporates a cyclic NP_3 backbone could be synthesized using knowledge gained from the chemistry of N_2P_2 and P_4 ring systems. It fills the gap between the congeneric compounds $[ClP(\mu\text{-}NR)]_2$ and $[ClP(\mu\text{-}PR)]_2$ (R = sterically demanding substituent), and thus contributes to the systematic development of nitrogen-phosphorus chemistry in general. The title compound was studied with respect to its formation *via* a labile aminodiphosphene, which readily underwent different rearrangement reactions depending on the solvent. All compounds were fully characterized by experimental and computational methods.

Four-membered ring systems composed of group 15 elements (pnictogens) have been in the focus of chemical research for almost 150 years:[1–6] When Michaelis and co-workers attempted to prepare diphenyldiphosphene Ph–P=P–Ph (**1Ph**) and chloro-(phenylimino)phosphane Ph–N=P–Cl (**2Ph**) in the late 19th century,[7,8] they obtained, although unbeknownst to them, the first cyclotetraphosphane $[PhP]_4$ (**4Ph**) and cyclodiphosphadiazane $[ClP(\mu\text{-}NPh)]_2$ (**5Ph**), which can be regarded as cyclic dimers of the intended products. The true structure of these compounds, however, was only recognized in the mid-20th century,[9–12] and only over the last 30 years it became apparent that the formal equilibrium between the acyclic monomer and cyclic dimer can be controlled by tuning the sterical demand of the substituents (Scheme 1).[13–19]



Scheme 1. Formal equilibrium between monomeric and dimeric EP systems depending on the sterical demand of the substituents (E = N, P; R = sterically demanding substituent; R' = organic substituent or (pseudo)halogen).

Consequently, with the development of sterically demanding substituents such as Mes* (2,4,6-tri-*tert*-butylphenyl) or Ter (2,6-dimesitylphenyl), it was possible to isolate highly reactive dipnictenes such as Mes*–P=P–Mes* (**1Mes***),[13,14] Ter–P=P–Ter (**1Ter**),[20] and Mes*–N=P–Cl (**2Mes***)[15] that are comparable to the original target molecules of Michaelis and co-workers. Notably, upon formal replacement of the Mes* moiety of **2Mes*** by the slightly less sterically demanding Ter substituent, again the four-membered ring system $[ClP(\mu\text{-}NTer)]_2$ (**5Ter**) is obtained,[21] rendering **2Mes*** the only known monomeric chloroiminophosphane to date (Scheme 2). As a result of this striking dependence on slight variations of substituent size, the chemistry of iminophosphanes and diphosphenes is nowadays intrinsically tied to the chemistry of the corresponding N_2P_2 and P_4 ring systems, respectively.



Scheme 2. Examples of monomeric dipnictenes and their corresponding cyclic dimers. The diphosphene **3Mes*** was possibly detected by *in situ* ^{31}P NMR spectroscopy,[22] however, the reported NMR data are inconclusive (cf. SI, p. S39). The synthesis of unprecedented **7Mes*** is presented in this publication.

Within this field of research, especially cyclodiphosphadiazanes of the type $[XP(\mu\text{-}NR)]_2$ (X = (pseudo)halogen, e.g. **5Ter**) were thoroughly investigated.[1–6] The (pseudo)halogen substituents allow for facile functionalization of the ring system, which is why these species have become versatile reagents in NP chemistry. Recently, we could show that a similar conceptual approach is valid for the heavier congeners, $[XP(\mu\text{-}PR)]_2$ (e.g. **6Mes***),[23–28] thus offering complementary access to the chemistry of cyclophosphanes, which was previously mainly investigated by methods of direct activation of white phosphorus (P_4).[29–31]

As indicated before, all these previous results have in common that the ring systems thus obtained are conceptually derived from monomeric iminophosphanes or diphosphenes. Hence, the cyclic dimers are always symmetric. However, to the best of our knowledge, *asymmetric* four-membered NP ring systems with halogen substituents are unprecedented to date. Consequently, we were interested in the synthesis of NP_3 ring

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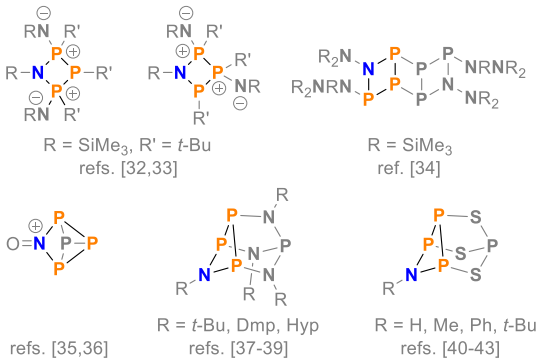
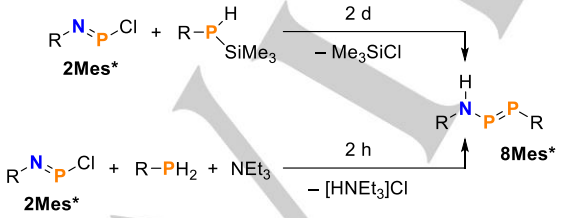
systems that can be regarded as a blend of the established N_2P_2 and P_4 cycles (**7Mes***, Scheme 2, bottom right).

Incidentally, even when regarding NP_3 ring systems in general, i.e. without a specific substitution pattern, only few examples are known. In addition, these incorporate λ^5 phosphorus centers[32,33] or are substructures of larger polycyclic compounds (Scheme 3),[34–43] which renders hitherto unknown, monocyclic NP_3 ring systems based on λ^3 phosphorus a particularly interesting target of research.



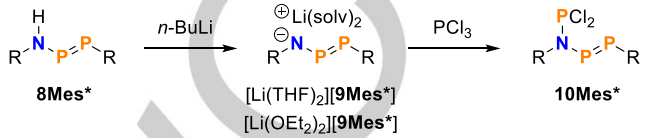
Scheme 3. Overview of previously reported compounds containing a cyclic NP_3 substructure (Dmp = 2,6-dimethylphenyl, Hyp = Tris(trimethylsilyl)silyl).

Our synthetic approach involved a step-wise assembly of the NP_3 skeleton starting from well-known monomeric NP building block Mes*NPCl (**2Mes***).[15] Conveniently, previous results had already shown that treatment of **2Mes*** with the secondary phosphane Mes*P(H)SiMe$_3$ yielded the aminodiphosphene Mes*PPN(H)Mes* (**8Mes***; Scheme 4, top);[44] however, due to steric bulk of the silyl substituent at the phosphane, the reaction was rather slow (ca. 2 days of reaction time). Therefore, an alternative base-assisted approach to synthesize **8Mes*** was developed, and indeed, treatment of **2Mes*** with the primary phosphane Mes*PH$_2$ in the presence of NEt$_3$ led to complete conversion after only two hours of stirring at ambient temperature (Scheme 4, bottom). [HNEt$_3$]Cl was easily filtered off and the product could be crystallized from hot benzene, giving yellow needles in 84 % yield.



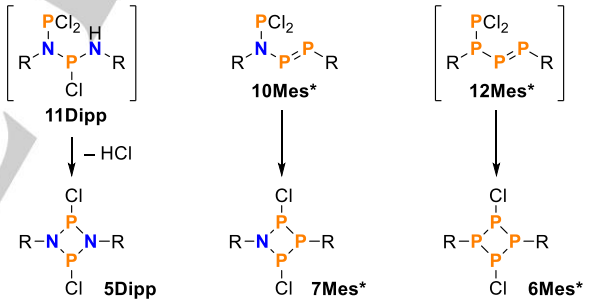
Scheme 4. The synthesis of **8Mes*** *via* base assisted HCl elimination proved to be considerably faster than the Me$_3$SiCl elimination route (R = Mes*).

In the next step, **8Mes*** was dissolved in THF, lithiated using *n*-BuLi according to a known procedure,[44] and then treated with PCl_3 to afford the aminodiphosphene Mes*PPN(PCl$_2$)Mes* (**10Mes***, Scheme 5), an open-chain isomer of the desired product **7Mes***. Initially, this procedure proved to be rather unselective and afforded many by-products. In fact, the diphosphene **10Mes*** was shown to be unstable in polar solvents such as THF (*vide infra*), which led to several side reactions. Nonetheless, when using less polar Et$_2$O for the lithiation step and subsequently reacting the isolated lithium salt [Li(OEt$_2$)$_2$][Mes*PPNMes*] ([Li(OEt$_2$)$_2$][**9Mes***]) with a solution of PCl_3 in non-polar *n*-pentane, **10Mes*** could be obtained in good yields (60 %).



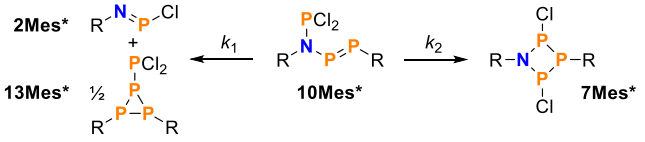
Scheme 5. Synthesis of **10Mes*** (R = Mes*). In non-polar solvents (Et$_2$O, *n*-pentane), the product could be obtained in 60 % yield.

Compound **10Mes*** is especially interesting, as it can be regarded as a constitutional isomer of the desired ring system **7Mes***. It is also closely related to the transient intermediates **11Dipp** (Dipp = 2,6-diisopropylphenyl) and **12Mes*** (Scheme 6), which were previously observed spectroscopically during the syntheses of [ClP(μ-NDipp)]$_2$ (**5Dipp**)[45] and [ClP(μ-PMes*)] (**6Mes***);[23] however, those intermediates could not be isolated.



Scheme 6. Open-chain intermediates that were observed during the syntheses of **5Dipp**, **6Mes*** and **7Mes***.[23,45]

Similarly to the known synthesis of the cyclotetraphosphane **6Mes*** *via* intermediate **12Mes***,[23] the isomerization of **10Mes*** to **7Mes*** was found to be favored in polar solvents such as THF or CH_2Cl_2 and was complete within eight hours (Scheme 7, Figure S14). After recrystallization from *n*-hexane, the ring system **7Mes*** could then be isolated in 29 % yield (*vide infra*). In contrast, dissolution of the precursor **10Mes*** in non-polar solvents such as benzene led to slow decomposition within one week, yielding a mixture of Mes*NPCl (**2Mes***) and [(Mes*P)$_2$μ-P(PCl$_2$)] (**13Mes***, Scheme 7). In comparison with calculated thermodynamic data (Figure 1), which favored the formation of **7Mes*** by *ca.* 9 kJ/mol (ΔG^{298K}) independently of the solvent, the observed reactivity implies that the reaction is under kinetic control depending on the polarity of the solvent. This is also in agreement with the experimentally determined large differences of the rate constants in benzene and THF (Scheme 7).



Scheme 7. Isomerization of **10Mes*** in different solvents: Benzene: k_1 = 5.9(2) × 10^{-6} s^{-1}, k_2 not observed. THF: k_1 = 6.07(14) × 10^{-5} s^{-1}, k_2 = 6.68(15) × 10^{-5} s^{-1} (cf. SI, p. S41).

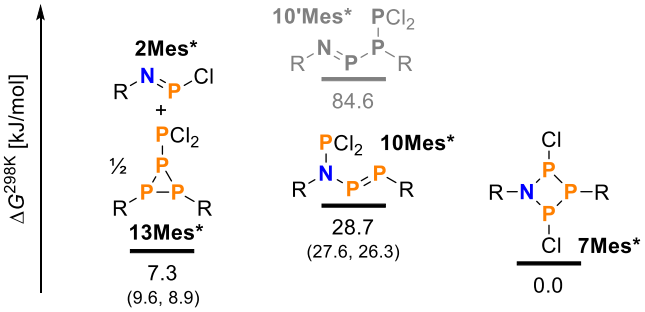


Figure 1. Calculated thermodynamic data of different formal isomers and rearrangement products of **10Mes*** in kJ/mol (PBE0/def2svp, R = Mes*). Data for solvents (THF, benzene) are given in brackets (PCM). **10'Mes*** is a hypothetical, open-chain isomer and was not observed experimentally.

Interestingly, **2Mes*** and **13Mes*** can be regarded as formal [2+2] cycloreversion products of the four-membered ring system **7Mes***, when considering that the cyclotriphosphane **13Mes*** represents a formal dimer of Mes*PPCl (**3Mes***). The *t*-Bu substituted derivative, **13tBu**, was previously reported;[46] the ^{31}P NMR data and especially the coupling constants are in good agreement. Moreover, the calculated ^{31}P NMR data of **13Mes*** corresponds well to the experimental spectrum (SI).

The ^{31}P NMR data of the intermediate products **8Mes***, [**9Mes***]$^-$ and **10Mes*** displayed typical characteristics of diphosphenes, that is, large chemical shifts in the low field region (318–486 ppm) as well as large, negative ^1J coupling constants (around −540 Hz, cf. SI).[47–49] Additionally, **10Mes*** exhibited a third signal (160.8 ppm, AMX spin system) indicative of a $-PCl_2$ functionality.[46,50–52] The four-membered ring system **7Mes*** was characterized by an AX_2 spin system (−26.4, 207.2 ppm; −174 Hz), which can be compared to the NMR data of the related compound **6Mes*** (A_2X_2: −8.1, 131.1 ppm; −217 Hz).[23]

Using Raman spectroscopy, the P–P double bonds in **8Mes***, [**9Mes***]$^-$ and **10Mes*** could be easily identified by the most intense signals in the corresponding spectra at 609, 592 and 615 cm^{-1}, respectively. The significant red-shift of the P–P valence vibration in [**9Mes***]$^-$ was attributed to distinct 3*c*4*e* π-bonding within the NPP unit and thus population of the antibonding π^*_{PP} orbital, as indicated by NBO[53] calculations (Figure 2). The same effect was less pronounced in **8Mes***, and almost negligible in **10Mes***. However, NBO calculations for the latter revealed a significant interaction of the LP at N with one of the antibonding σ^*(P–Cl) orbitals, which acted as a π acceptor orbital (Figure 2, bottom left). This weakening of one P–Cl bond emphasizes the instability of compound **10Mes*** with respect to the previously discussed isomerization reactions. Also, the electronic situation is in contrast to related compounds of heavier pnictogens such as TerNNN(ECl_2)Ter (E = P, As, Sb, Bi), TerNPN($SbCl_2$)Ter or TerPAsN($SbCl_2$)Ter, where the coplanar σ^*(P–Cl) orbital acted as a σ acceptor for the in-plane LP at the opposite N or P atom.[54–56]

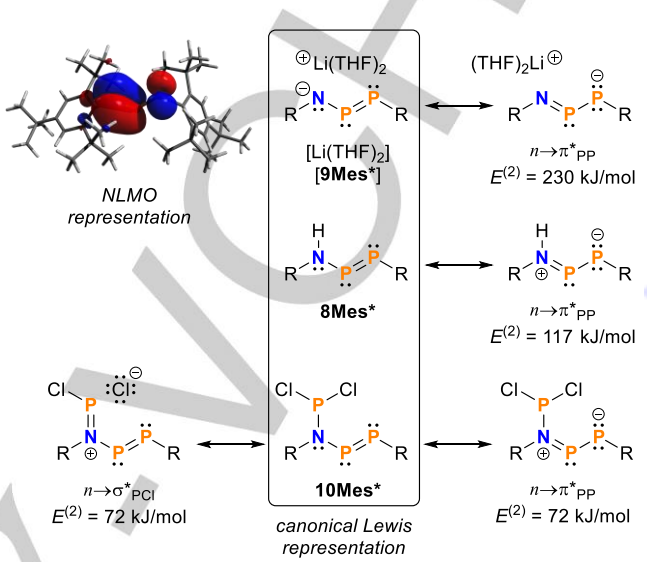


Figure 2. Principal delocalizations of the lone pair (*n*) at nitrogen in the NBO picture. In [$Li(THF)_2$][**9Mes***], the NPP π-bonding system is best described as a 3*c*4*e* bond (cf. Natural Localized Molecular Orbital representation, top left). This effect is less pronounced in **8Mes*** and **10Mes***. The latter, however, displays significant population of one of the antibonding σ^*(P–Cl) orbitals.

The different bonding situations were found to be well reflected in the molecular structures of compounds [$Li(THF)_2$][**9Mes***] and **10Mes*** (Figure 3): In agreement with a localized P–P double bond, the latter displayed a short P1–P2 (2.0353(5) Å) and a long P2–N1 interaction (1.751(1) Å), whereas the former exhibited a slightly longer P1−P2 bond length (2.064(1) Å) and a significantly shortened P2−N1 distance (1.625(1) Å), which corresponded well to the description as a 3*c*4*e* π bond (cf. Σr_{cov}(P=P) 2.04 Å; Σr_{cov}(P=N) 1.62 Å; Σr_{cov}(P–N) 1.82 Å).[57] Moreover, the P3−N1 bond length in **10Mes*** was significantly shortened (1.687(1) Å), while the P3–Cl2 bond, which was nearly perpendicular to the NPP plane, was elongated (2.1062(5) Å) in comparison to the coplanar P3–Cl1 bond (2.0638(5) Å). This observation nicely underlines the contribution of the left Lewis representation of **10Mes*** in Figure 2.

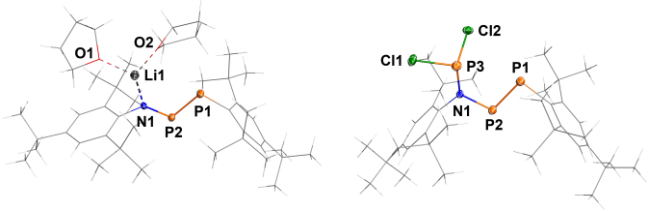


Figure 3. Molecular structures of [$Li(THF)_2$][**9Mes***] and **10Mes*** in the crystal. Ellipsoids set at 50 % probability (123 K). To the best of our knowledge, [$Li(THF)_2$][**9Mes***] is the first structurally characterized azadiphosphenide.

The Li–N distance in [Li(THF)$_2$][**9Mes***] was found to be 1.982(3) Å. According to DFT calculations,[58] this interaction is mostly electrostatic; thus, the compound is best described as a contact ion pair. The NPA partial charges at N and Li are −1.13 *e* and +0.89 *e*, respectively, and the overall charge of the [**9Mes***] moiety amounts to −0.93 *e*. Hence, the formal charge transfer between anion and cation is very low (0.07 *e*).

The solid-state structure of the desired ring system **7Mes*** (Figure 4, left) comprised three independent molecules in the asymmetric unit (space group $P\bar{1}$), as well as two molecules of *n*-hexane per unit cell. All three molecules displayed similar structural parameters, so only the average values shall be discussed: The four-membered ring system adopted a rather flat structure (av. fold angle: 164°), while the Cl substituents were arranged in *cis*-position. All P–P bond lengths (av. 2.255(2) Å) lay in the range of typical single bonds (cf. Σr_{cov}(P–P) 2.22 Å)[57] and the N–P bond lengths (av. 1.720(1) Å) corresponded to polarized N–P single bonds. The P–Cl bond lengths differed slightly, with one shorter (av. 2.105(1) Å) and one longer bond (av. 2.131(3) Å, cf. Σr_{cov}(P–Cl) 2.10 Å). The coordination environment at the N atom was nearly planar (av. Σ(∠N) 355°), whereas the P atoms were embedded in typical trigonal pyramidal substitution environments. Even though computations predicted a similarly stable isomer with *trans* arrangement of the Cl substituents (ΔG^{298K} = 3.3 kJ/mol), solely the *cis* isomer of **7Mes*** was observed.

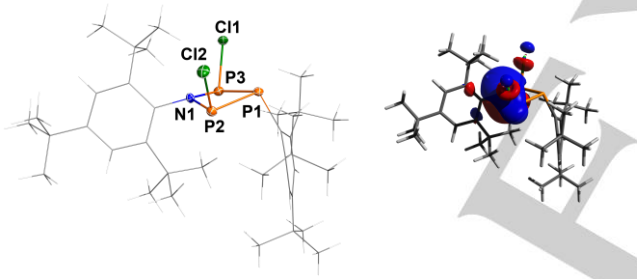


Figure 4. Left: Molecular structure of **7Mes*** in the crystal. Ellipsoids set at 50 % probability (123 K). Right: NLMO representation of negative hyperconjugation of the nitrogen LP into σ*(P–Cl) orbitals.

The structural parameters relate well to analogous N_2P_2 or P_4 ring systems, e.g. **5Ter** and **6Mes***:[21,23] In case of **5Ter**, the central N_2P_2 ring system was perfectly planar, with either *cis*- or *trans*-arrangement of the Cl substituents. The cyclophosphane **6Mes***, on the other hand, incorporated a distinctly butterfly-shaped cyclic scaffold with fold angles in the range of 120–143° and *cis*-arrangement of the Cl atoms. The P–P, P–N and P–Cl bond lengths were very similar in all three compounds. Hence, the NP_3 ring system **7Mes*** blends nicely into the previously observed structural trends.

NBO analysis of the bonding situation showed that the LP at N was partly delocalized over the NP_3 ring system by negative hyperconjugation into both σ*(P–Cl) orbitals (Figure 4, right). Due to the slightly angled structure of the Mes* substituent at N, the calculated stabilization energy was somewhat larger in case of the P3–Cl1 moiety (73.6 *vs*. 63.6 kJ/mol), which corresponds well to the longer P3–Cl1 bond length in the experimental molecular structure. Also, the weakening of the P–Cl bonds may lead to interesting reactivity, which will be investigated in detail in future studies.

In conclusion, the novel NP_3 ring system **7Mes*** could be synthesized in a stepwise reaction *via* interesting diphosphene intermediates, such as the first structurally characterized azadiphosphenide [Mes*–N–P=P–Mes*]$^-$ in [Li(THF)$_2$][**9Mes***]. **7Mes*** comprises an "asymmetric" NP_3 ring system and therefore fills the gap between known, symmetric N_2P_2 and P_4 cycles, which were previously synthesized from precursors of their respective monomers. Intriguingly, the diphosphene **10Mes***, an open-chain isomer of **7Mes***, tends to decompose to NP or PP fragments, which again can be regarded as building blocks for the respective N_2P_2 or P_4 cycles. These findings enhance the systematic understanding of nitrogen-phosphorus chemistry and open up interesting research possibilities for future studies in this field.

Experimental Section

Detailed information on the synthesis of all starting materials and products, including a full set of analytical data, is given in the Supporting Information. CCDC #1551842–1551844 contain the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre.

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Keywords: phosphorus chemistry • nitrogen chemistry • four-membered ring systems • structure elucidation • DFT calculations

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[58] Detailed information on computational studies can be found in the Supporting Information.

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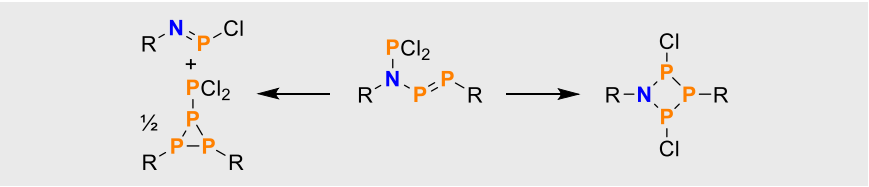

NP_3 ring system: Starting from a highly reactive amino-diphosphene, a dichloro-cycloazatriphosphane (Scheme, right) could be synthesized and fully characterized. This new ring system can be regarded as a congener of $[XP(\mu\text{-}NR)]_2$ and $[XP(\mu\text{-}PR)]_2$ systems and therefore contributes to a systematic development of NP chemistry.

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Dichloro-cycloazatriphosphane — the missing link between N_2P_2 and P_4 ring systems in the systematic development of NP chemistry