

Ring Compounds

A Systematic Survey of the Reactivity of Chlorinated N_2P_2 , NP_3 and P_4 Ring SystemsJonas Bresien,^{*,[a]} Liesa Eickhoff,^[a] Axel Schulz,^{*,[a, b]} Tim Suhrbier,^[a] and Alexander Villinger^[a]

Abstract: The reactivity of the four-membered NP_3 ring system $[RN(\mu-PCl)_2PR]$ ($R = \text{Mes}^* = 2,4,6\text{-tri-}t\text{-butylphenyl}$) towards Lewis acids, Lewis bases, and reducing agents was investigated. Comparisons with the literature-known, analogous cyclic compounds $[CIP(\mu-NR)]_2$ ($R = \text{Ter} = 2,6\text{-dimesityl-}$

phenyl) and $[CIP(\mu-PR)]_2$ ($R = \text{Mes}^*$) are drawn, to obtain a better systematic understanding of the reactivity of cyclic NP species. Apart from experimental results, DFT computations are discussed to further the insight into bonding and electronic structure of these compounds.

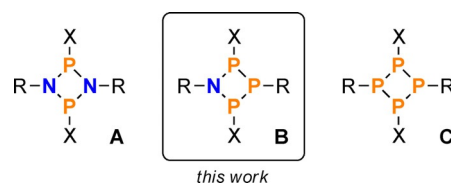
Introduction

Phosphorus chemistry nowadays plays an important role in a variety of research domains, such as biochemistry, organic and inorganic chemistry, catalysis, and materials science.^[1–6] A great variety of chemical processes rely on phosphorus compounds, both in nature^[7] and in industrial chemistry. For example, phosphane-based ligands find widespread use in transition metal complexes that are being applied for large-scale industrial processes, such as hydroformylation reactions or syntheses involving C–C and C–N bond formation.^[3]

It is therefore desirable to further the systematic development of phosphorus chemistry, particularly when regarding the fact that phosphorus is often dubbed a “carbon copy”.^[8] The chemistry of carbon is, of course, well and systematically investigated, and there is a plethora of different types of reactions that can be used to synthesize a large variety of different classes of organic compounds. It is probably without dispute that the same level of understanding has not yet been reached in case of phosphorus chemistry, which is why we are interested in a systematic investigation of phosphorus-based compounds.

In particular, our group has a long-standing interest in cyclic oligophosphanes and aminophosphanes. Such ring systems

show a diverse reaction behaviour and have therefore attracted the interest of many researchers during the past few decades.^[9–15] Among these classes of compounds, especially four-membered N_2P_2 ring systems were thoroughly studied, as detailed in a number of review articles.^[16–20] Out of the many possible substitution patterns at the N_2P_2 ring system, those species with halogen substituents (e.g. compounds of the type $[XP(\mu-NR)]_2$ (**A**, $X = \text{halogen}$, $R = \text{sterically demanding group}$; Scheme 1) were shown to be easily functionalized by halide abstraction, substitution reactions, or reduction, rendering them worthwhile building blocks in phosphorus-nitrogen chemistry (Scheme 2).^[21–26]



Scheme 1. Four-membered N_2P_2 , NP_3 and P_4 ring systems ($R = \text{sterically demanding substituent}$, $X = (\text{pseudo})\text{halogen}$).

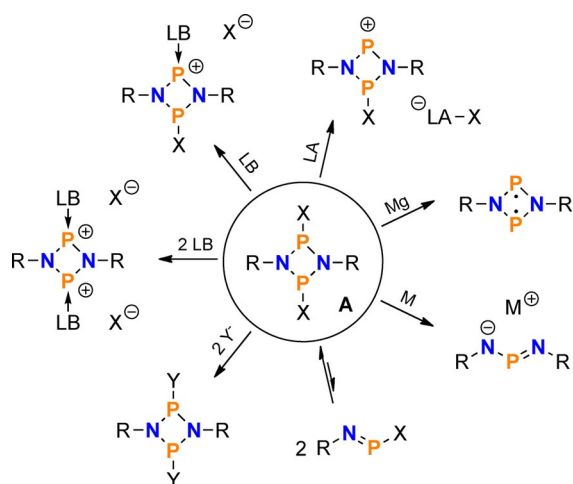
More recently, we became interested in the reactivity of cyclic phosphanes of the type $[XP(\mu-PR)]_2$ (**C**),^[27–31] which had barely been investigated prior to our work. In particular, we were interested in how the reaction behaviour of these species would compare to the congeneric N_2P_2 ring systems (**A**), in view of the formal replacement of the two N atoms by phosphorus. It was found that the P_4 ring system **C** displayed a tendency to stabilize positive charges (induced by halide abstraction or substitution) by rearrangement reactions associated with the formation of transannular P–P bonds (Scheme 3).^[32–35] The N_2P_2 ring system **A**, on the other hand, was shown to stabilize positive charges by delocalization of π -electron density within the ring, due to the p -type character of the lone pair of electrons (LP) at N. In contrast, the LP at phosphorus in the P_4

[a] Dr. J. Bresien, L. Eickhoff, Prof. Dr. A. Schulz, T. Suhrbier, Dr. A. Villinger
Institut für Chemie, Universität Rostock
Albert-Einstein-Str. 3a, 18059 Rostock (Germany)
E-mail: jonas.bresien@uni-rostock.de

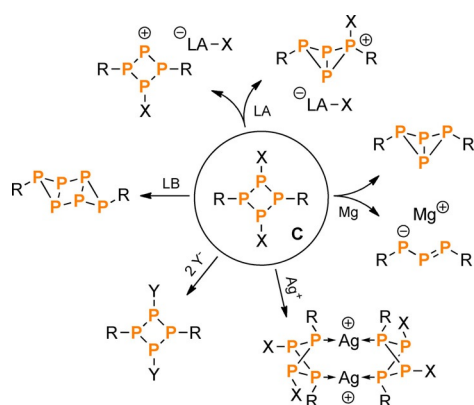
[b] Prof. Dr. A. Schulz
Abteilung Materialdesign, Leibniz-Institut für Katalyse an der
Universität Rostock e.V., Albert-Einstein-Str. 29a, 18059 Rostock (Germany)
E-mail: axel.schulz@uni-rostock.de

Supporting information and the ORCID identification number(s) for the author(s) of this article can be found under:
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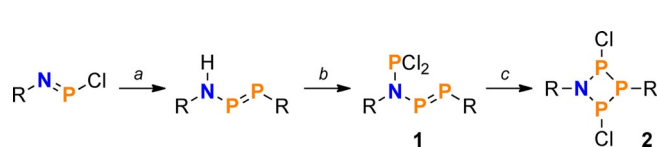
Scheme 2. Reactivity of A (R = sterically demanding substituent, LB = Lewis base; LA = Lewis acid; M = Mg, K; X, Y = Cl, OTf, N₃, etc.).



Scheme 3. Reactivity of C (R = sterically demanding substituent, LB = Lewis base; LA = Lewis acid; X = Cl; Y = C₆F₅, see below).

ring system has a large s character, which hampers this kind of electronic interaction.

The apparent differences in reactivity prompted us to investigate NP₃ ring systems (B, Scheme 1),^[36] which incorporate only one nitrogen atom for electronic stabilization and can formally be regarded as a blend of N₂P₂ and P₄ ring systems. Particularly, we were interested in the reactivity of ring system B towards Lewis acids, Lewis bases, nucleophiles, as well as reducing agents. The synthesis of the NP₃ ring system [Mes*N(μ-PCl)₂PMes*] (2; Mes* = 2,4,6-tri-*tert*-butylphenyl, Scheme 4) was recently published^[36] and served as a starting point for the investigations reported in this paper.

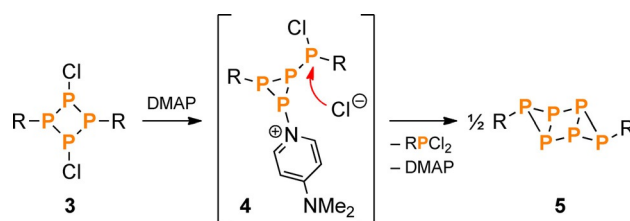


Scheme 4. Synthesis of 2 (R = Mes*) starting from Mes*NPCl^[37] (a: Mes*PH₂, NEt₃; b: *n*BuLi, PCl₃, -80 °C; c: THF).

Results and Discussion

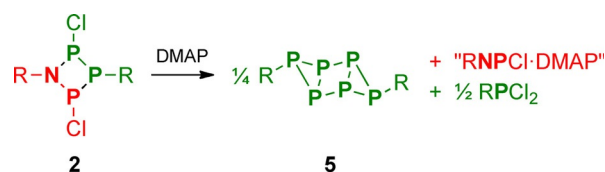
To begin with, the synthesis of 2 could be optimized using a MeCN/CH₂Cl₂ mixture instead of THF for the isomerization step (Scheme 4c). As reported previously, the isomerization of 1 can lead to different products depending on the polarity of the solvent.^[36] Since more polar media favour the formation of the desired ring system 2, MeCN seemed a reasonable choice of solvent; however, 1 and 2 were only sparingly soluble in MeCN. After addition of CH₂Cl₂ to the suspension, the starting material slowly dissolved. Letting the mixture rest overnight afforded large block-shaped crystals of the product in 73% yield. A series of ³¹P NMR spectra was recorded to monitor the progress of the isomerization. The spectra show that almost no side products were formed in the MeCN/CH₂Cl₂ mixture (Figure S3, Supporting Information). Using this improved protocol, compound 2 could be synthesized on multi-gram scale.

In a first series of experiments, the reactivity of the NP₃ ring system 2 towards the Lewis base DMAP (4-dimethylaminopyridine) was investigated. As previously shown, the reaction of DMAP with the P₄ ring system [ClP(μ-PMes*)]₂ (3, type C) led to rearrangement of the P–P bonding system and elimination of Mes*PCl₂, yielding the tricyclic hexaphosphane 5 in nearly quantitative yields (Scheme 5).^[33] It was therefore of interest to



Scheme 5. Reaction of 3 with DMAP (R = Mes*).^[33]

see if a similar reaction behaviour could be observed in case of the NP₃ ring system 2, possibly yielding an analogous tricyclic structure with an N-capped P₄ ring system. Astonishingly, though, the isolated product of the reaction of 2 with DMAP was the same tricyclic P₆ system (5), indicating that the N atom had formally been eliminated from the starting material (Scheme 6). To shed light on the reaction path, in situ ³¹P NMR spectra were collected, which showed that Mes*PCl₂ and presumably Mes*NPCl·DMAP (pp. S19ff) were formed as further products of the reaction. Hence, the formation of 5 can be understood in terms of a formal cycloreversion of 2 (Scheme 6), that is, the products can formally be derived from the monomeric building blocks of 2, Mes*NPCl and "Mes*P(=O)Cl" (which

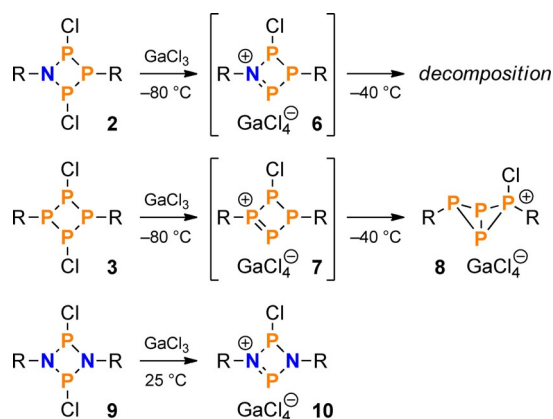


Scheme 6. Reaction of 2 with DMAP (R = Mes*).

dimerizes to $[\text{CIP}(\mu\text{-PMes}^*)]_2$ (**3**), cf. Scheme 5). However, as no intermediates besides **4** could be observed in the ^{31}P NMR spectra (Figure S6), the exact mechanism of the reaction remains unclear.

It is worthy to note that the reaction of the acyclic NP_3 compound **1** with DMAP led to a similar outcome, which indicates conversion of **1** to **2** under reaction conditions.

In a next set of experiments, the reactivity of the NP_3 ring system **2** towards Lewis acids was investigated. As GaCl_3 had proved to be a suitable reagent for selective chloride abstraction,^[38–44] it was chosen as a model substrate to investigate this type of reaction. As expected, low temperature ^{31}P NMR spectroscopy revealed that abstraction of one chloride ion from the ring system led to the formation of a phosphonium salt (**6**; Scheme 7, top), which is analogous to those observed in case of the congeneric N_2P_2 and P_4 ring systems (**7**, **10**; Scheme 7).



Scheme 7. Reaction of NP_3 ring system **2** with GaCl_3 ($\text{R} = \text{Mes}^*$), in comparison with the reactivities of P_4 and N_2P_2 ring systems **3** ($\text{R} = \text{Mes}^*$)^[32] and **9** ($\text{R} = \text{Ter} = 2,6\text{-dimesitylphenyl}$).^[23]

Similarly to tetraphosphenium salt **7**,^[32] a solution of the azatriphosphenium salt **6** was only stable at low temperatures below -40°C , as evidenced by variable temperature NMR spectra (Figure S8). In the ^{31}P NMR spectrum, **6** was identified by an AMX spin system (Figure 1) with a characteristic, downfield-shifted X part, due to the positive charge and strongly polarized NP double bond ($\delta(\text{P}_\text{X}) = +446.4$ ppm; cf. **7**: $+358.9$,^[32] **10**: $+366.6$ ppm).^[23] All observed NMR shifts and coupling constants are in good agreement with theoretical data (Table 1).

Contrary to its N_2P_2 and P_4 congeners **7** and **10**, the NP_3 species **6** decomposed to an unidentified mixture of products upon warming. At first glance, this might seem unexpected, especially in view of the fact that the diazadiphosphenium salt **10** is perfectly stable up to well beyond 200°C .^[23] In case of the NP_3 species **6**, the single N atom is apparently not sufficient to stabilize the formal phosphonium centre by donation of π -electron density into the vacant p -orbital at P. On the other hand, while the P_4 system **7** can stabilize itself by formation of a transannular P–P bond and concomitant pyramidalization of all P atoms, the same is not true of the NP_3 ring system **6**, as this would entail a high ring strain at the N atom,

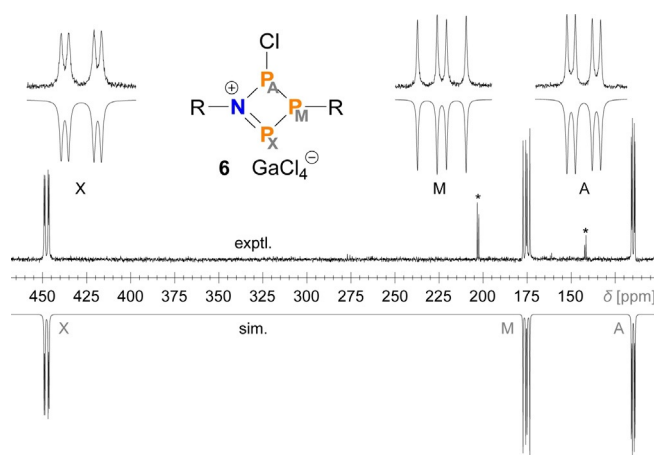
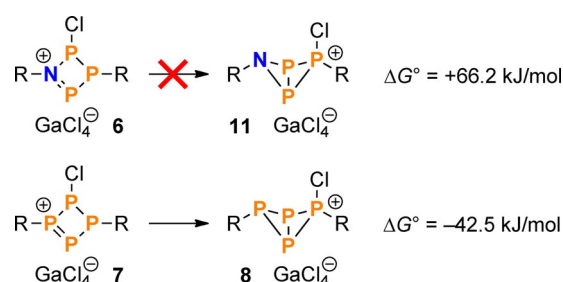


Figure 1. Experimental and simulated ^{31}P NMR spectrum (-70°C) of the reaction between **2** and GaCl_3 showing the formation of phosphonium salt **6** ($\text{R} = \text{Mes}^*$; starting material and by-products indicated by asterisks).

Table 1. Experimental ^{31}P NMR data of **6** (AMX spin system). Calculated values (PBE0-D3/def2-SVP, cf. SI) are given in brackets.

	δ [ppm]	J [Hz]	
		A	M
A	114.1 (105.7)		
M	175.4 (126.3)	-317 (-273)	
X	446.4 (442.7)	$+107$ ($+69$)	-470 (-442)

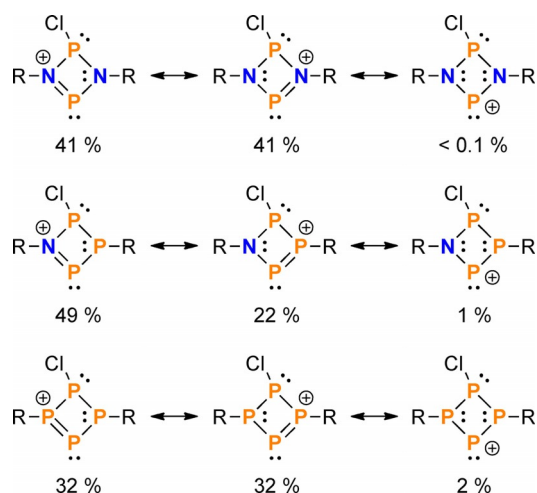
which is energetically unfavourable.^[45,46] Consequently, the bicyclic NP_3 isomer **11** is calculated to be much higher in energy than the phosphonium isomer **6** (Scheme 8), whereas the isomerization of the P_4 system **7** to the bicyclic phosphino-phosphonium salt **8** is thermodynamically favoured.



Scheme 8. Calculated Gibbs energies for the isomerization of the cations of compounds **6** and **7** (PBE0-D3/def2-SVP).

To better understand the differences in bonding within the cations of **6**, **7**, and **10**, Natural Resonance Theory (NRT) calculations on model cations (with $\text{R} = \text{H}$) were performed. For each species, a total of about 45 resonance structures was considered, most of which describe bond polarization within the ring or negative hyperconjugation of the LPs at Cl into the ring system. To simplify the discussion, only the two most important contributions to the Lewis resonance Scheme, as well as the Lewis structure with an electron sextet at the formal

phosphenium centre will be considered in the following (Scheme 9). Two trends can be derived, which underline the observed reactivity: Firstly, the overall contribution of the two most important Lewis structures (with NP or PP double bonds,



Scheme 9. Some Lewis resonance structures of model phosphenium cations ($R=H$) as well as their respective weights from NRT analysis.

respectively) decreases along the series N_2P_2 , NP_3 , P_4 ; that is the formal phosphenium is best stabilized by π -type interactions in the N_2P_2 cation, and least stabilized in the P_4 derivative. Secondly, the weight of the resonance structure with an electron sextet at the formal phosphenium increases from N_2P_2 to P_4 , formally rendering the latter the most reactive derivative. This is corroborated by the fact that the isomerization of the tetraphosphenium salt **7** to the bicyclic isomer **8** proceeded even at -80°C .^[32]

As with the P_4 congener **7**, all attempts to crystallize the azatriphosphenium salt **6** at low temperatures remained unsuccessful. In two instances, a few crystals of two different decomposition products could be isolated and studied by single crystal X-ray diffraction (SC-XRD). In both cases, a *t*Bu group of the Mes^* moiety had been transferred onto another molecular fragment or solvent molecule, indicating decomposition of the sterically demanding substituent (Figure 2). Cleavage of *t*Bu groups from Mes^* substituents is not uncommon in the presence of Lewis acids (or by thermal treatment),^[47–51] thus demonstrating the high Lewis acidity of salt **6**.

Next, we were interested in demonstrating nucleophilic substitution at the NP_3 ring system **2**. By analogy with the congeneric N_2P_2 ring system $[\text{CIP}(\mu\text{-NDipp})]_2$ (Dipp = diisopropylphenyl),^[52] the reaction of **2** with AgC_6F_5 resulted in precipitation of AgCl and formation of $[\text{Mes}^*\text{N}(\mu\text{-PC}_6\text{F}_5)_2\text{PMes}^*]$ (**12**, Scheme 10). After filtration, the latter could be crystallized from $\text{CH}_2\text{Cl}_2/\text{MeCN}$ to give yellow, block shaped crystals suitable for SC-XRD (Figure 3, left; yield of isolated substance: 48%).

The molecular structure of **12** revealed a flattened NP_3 ring system (fold angle:^[29,53] $164.04(8)^\circ$) with NP and PP bond lengths that correspond to somewhat shortened NP and slightly elongated PP single bonds, respectively (cf. $\Sigma r_{\text{cov}}(\text{N-P}) =$

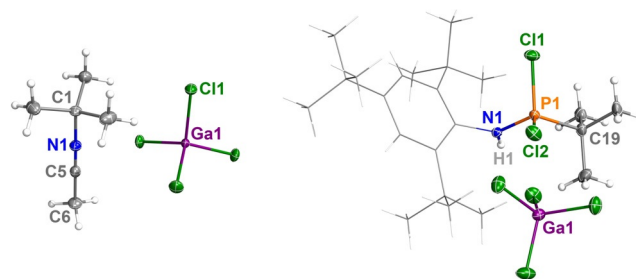
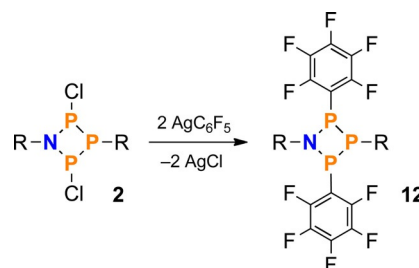


Figure 2. Molecular structures of the decomposition products $[\text{MeCNtBu}][\text{GaCl}_4]$ (left) and $[\text{Mes}^*\text{N}(\text{H})\text{PCl}_2\text{tBu}][\text{GaCl}_4]$ (right) in the crystal. Ellipsoids are set at 50% probability (123 K). Selected bond lengths (\AA) and angles ($^\circ$): $[\text{CH}_3\text{CNtBu}][\text{GaCl}_4]$ N1-C1 1.479(3), N1-C5 1.129(3), C5-N1-C1 178.2(2), N1-C5-C6 180.0(3), C1-N1-C5-C6 180.0; $[\text{Mes}^*\text{N}(\text{H})\text{PCl}_2\text{tBu}][\text{GaCl}_4]$ N1-P1 1.604(2), N1-H1 0.77(3), P1-C19 1.815(3), P1-Cl1 1.9798(9), N1-P1-C19 112.1(1), N1-P1-Cl1 111.40(9), C19-P1-Cl1 109.8(1), C1-N1-P1-C19 $-179.4(2)$.



Scheme 10. Reaction of **2** with AgC_6F_5 ($R = \text{Mes}^*$). Analogous reactions were observed for congeneric N_2P_2 ^[52] and P_4 species.

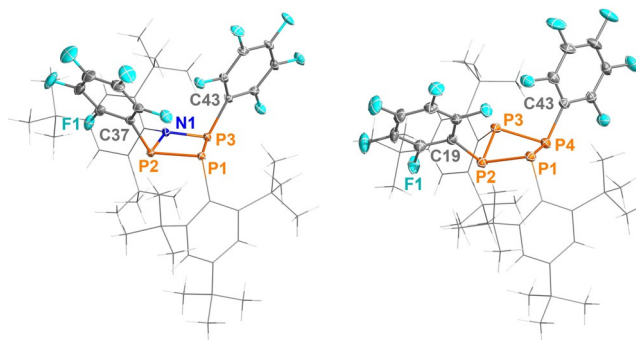


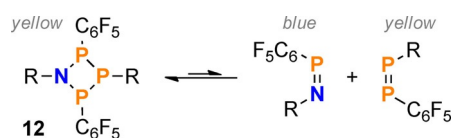
Figure 3. Molecular structures of **12** (left) and **13** (right) in the crystal. Ellipsoids are set at 50% probability (123 K and 173 K, respectively). Selected bond lengths (\AA) and angles ($^\circ$): **12** P1-P2 2.2461(6), P1-P3 2.2532(6), P2-N1 1.744(1), P2-C37 1.884(2), P3-N1 1.742(1), P3-C43 1.888(2), P2-P1-P3 76.09(2), N1-P2-P1 88.29(5), N1-P3-P1 88.12(5), P3-N1-P2 105.39(7), P1-P2-P3-N1 $-164.04(8)$; **13** P1-P2 2.2471(8), P1-P4 2.2611(9), P2-C19 1.853(2), P2-P3 2.1949(9), P3-P4 2.2367(8), P4-C43 1.858(2), P2-P1-P4 84.37(3), P3-P2-P1 88.99(3), P2-P3-P4 86.17(3), P3-P4-P1 87.61(3), P1-P2-P4-P3 $-142.45(4)$.

1.82 \AA ; $\Sigma r_{\text{cov}}(\text{P-P}) = 2.22 \text{ \AA}$).^[54] The nitrogen atom is located in a nearly planar coordination environment ($\Sigma(\angle \text{N}) = 352.8(3)^\circ$), whereas the phosphorus atom P1 is strongly pyramidalized ($\Sigma(\angle \text{P}) = 277.2(1)^\circ$). These structural parameters compare well with those of the starting material (**2**).^[36]

Since the reactivity of the P_4 ring system **3** towards AgC_6F_5 had not been reported previously, we also treated a solution of **3** with AgC_6F_5 , resulting in the corresponding P_4 ring system $[\text{F}_5\text{C}_6\text{P}(\mu\text{-PMes}^*)]_2$ (**13**, Figure 3, right). Its crystal structure could

be determined by SC-XRD. While the overall molecular structure is quite similar to that of its NP_3 congener (**12**), compound **13** exhibits two Mes^* -bound P atoms in a pyramidal coordination environment. Hence, the P_4 ring system adopts a much more puckered conformation with a fold angle of $142.45(4)^\circ$, which corresponds nicely to the experimental fold angle of the P_4 ring system in the starting material **3** ($120\text{--}143^\circ$ depending on the modification).^[29]

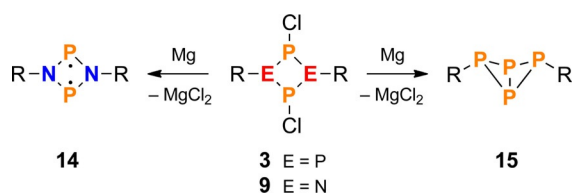
Both **12** and **13** displayed complex heteronuclear coupling patterns in the ^{31}P and ^{19}F NMR spectra. Additionally, the NP_3 ring system **12** exhibited various broadened signals due to hindered rotation of the C_6F_5 substituents (Figure S9). It is worthy to note that a yellow solution of **12** in CH_2Cl_2 started to turn green after one day, which was accompanied by the appearance of additional signals in the ^{31}P NMR spectrum. These signals could be assigned to the [2+2] cycloreversion products of the NP_3 ring system **12**, that is, (*Z*)- $\text{Mes}^*\text{P}=\text{PC}_6\text{F}_5$ ($\delta(^{31}\text{P}) = 381.2, 568.7$ ppm; $J = -557$ Hz) and (*Z*)- $\text{Mes}^*\text{N}=\text{PC}_6\text{F}_5$ ($\delta(^{31}\text{P}) = 361.7$ ppm)^[52] (Scheme 11, see also Figure S10). Computed



Scheme 11. Cycloreversion of **12** in solution ($\text{R} = \text{Mes}^*$). Due to the blue colour of (*Z*)- $\text{Mes}^*\text{N}=\text{PC}_6\text{F}_5$, the mixture appears green. The equilibrium ratio between the ring system **12** and the cycloreversion products is about 5:1:1.

^{31}P NMR data corroborate the assignment ((*Z*)- $\text{Mes}^*\text{P}=\text{PC}_6\text{F}_5$: 373.7, 525.8 ppm, -507 Hz; (*Z*)- $\text{Mes}^*\text{N}=\text{PC}_6\text{F}_5$: 372.8 ppm). The same type of reactivity was previously discussed for “symmetric” N_2E_2 ($\text{E} = \text{pnictogen}$) ring systems that can be regarded as dimers of iminopnictanes ($\text{RN}=\text{ER}'$).^[21,40,55] The equilibrium between monomeric and dimeric species was shown to depend on the size of the substituents R and R' .

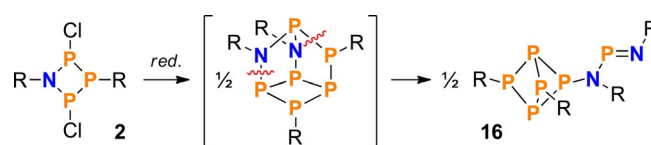
Lastly, the reduction of the NP_3 ring system **2** was of particular interest, especially when considering that the congeneric N_2P_2 species **9** and P_4 species **3** yielded two very different reduction products (Scheme 12). While the former can be reduced to a singlet biradical without a transannular PP bond (**14**),^[26] reduction of the latter leads selectively to the formation of a P_4 butterfly with a transannular PP bond (**15**).^[34] This can be understood in terms of π -electron delocalization, as detailed above, or ring strain at the nitrogen atom which pre-



Scheme 12. Reduction of N_2P_2 (**9**) and P_4 ring systems (**3**) leads to different types of products, namely the open shell singlet biradical **14** in case of $\text{E} = \text{N}$, and the closed shell [1.1.0]-bicyclic species **15** in case of $\text{E} = \text{P}$.

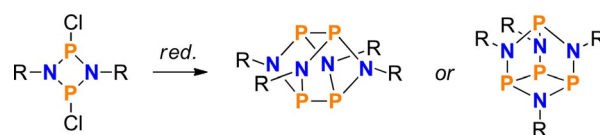
vents the N_2P_2 species from pyramidalization.^[46] In any case, it seemed interesting to explore which type of stabilization (planarization vs. pyramidalization) would predominate in the NP_3 case.

To that end, compound **2** was reduced using activated Mg chips, by analogy with the reduction of **3** and **9**.^[26,34,56] This led to a mixture of products, which—to our surprise—contained the bicyclic tetraphosphane $\text{Mes}^*\text{P}_4\text{Mes}^*$ (**15**)^[57] as one of the main components, indicating a formal cycloreversion of the NP_3 ring system into NP and PP fragments. To further investigate the formation of the bicyclic tetraphosphane **15**, $\text{Cp}_2\text{Ti}(\text{BTMSA})$ ^[58] (BTMSA = bis(trimethylsilyl)acetylene) was employed as a milder reducing agent. Indeed, this procedure facilitated the isolation of a few crystals of an unusual N_2P_6 cage compound with a bicyclo[1.1.1]pentaphosphane scaffold (**16**, Scheme 13). Compound **16** may be regarded as a dimer of the



Scheme 13. Formally, cage compound **16** ($\text{R} = \text{Mes}^*$) can be derived from a β -cage-type structure, which itself may be viewed as a dimer of $\text{Mes}^*\text{NP}_3\text{Mes}^*$ (red. = reduction).

biradical $\text{Mes}^*\text{NP}_3\text{Mes}^*$ (**17**, p. S62f), which is predicted to be only slightly less stable than its [1.1.0]-bicyclic isomer (**18**, $\Delta G^\circ = 14.2$ kJ mol $^{-1}$ at DLPNO-CCSD(T)/def2-TZVP//PBE-D3/def2-SVP level of theory, see below). Formal dimerization of congeneric N_2P_2 biradicals was already reported for species with small substituents R , leading to the formation of α - or β -cage structures with an N_4P_4 scaffold (Scheme 14).^[59–61]



Scheme 14. With small substituents (e.g. $\text{R} = t\text{Bu}$), the reduction of N_2P_2 ring systems leads to the formation of N_4P_4 cage compounds (left: α -, right: β -cage) that can be regarded as dimers of the respective biradicals $[\text{P}(\mu\text{-NR})]_2$.^[59–61]

The molecular structure of **16** could be elucidated by SC-XRD (Figure 4). All PP bond lengths within the bicyclo[1.1.1]-pentaphosphane scaffold correspond to slightly elongated PP single bonds (cf. $\Sigma r_{\text{cov}}(\text{P}–\text{P}) = 2.22$ Å).^[54] The N1–P6 distance corresponds to a polarized NP single bond, whereas the N2–P6 distance is in the range of a typical NP double bond (cf. $\Sigma r_{\text{cov}}(\text{N}–\text{P}) = 1.82$, $\Sigma r_{\text{cov}}(\text{N}=\text{P}) = 1.62$ Å). It is worthy to note that the bond angles at the P atoms within the P_5 cage are quite small (P1, P2, P3: avg. $77.8(2)^\circ$; P4, P5: avg. $84(1)^\circ$), as expected for a polycyclic P_n structure. When viewed along the P4–P5 axis, all substituents are bent to the left, thus minimizing the repulsion between the LPs at P1, P2, and P3. To the best of our

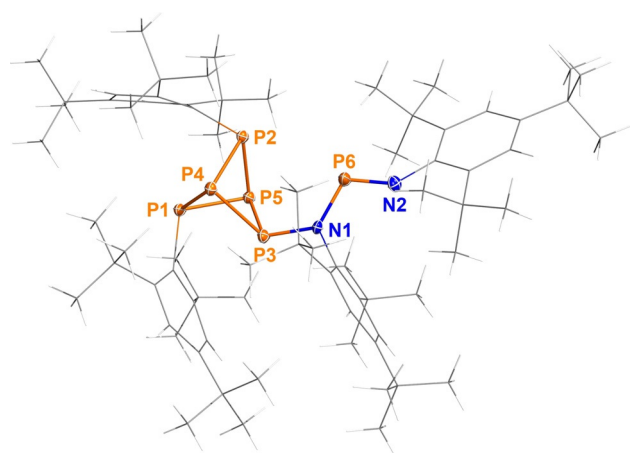


Figure 4. Molecular structure of **16** in the crystal. Ellipsoids are set at 50% probability (123 K). Selected bond lengths (Å) and angles (°): P1–P4 2.245(1), P1–P5 2.274(1), P2–P4 2.250(1), P2–P5 2.276(1), P3–P4 2.270(1), P3–P5 2.225(1), P3–N1 1.759(3), P6–N1 1.702(3), P6–N2 1.544(3), P4–P1–P5 77.66(4), P4–P2–P5 77.50(4), P5–P3–P4 78.14(4), P1–P4–P2 84.80(4), P1–P4–P3 81.23(4), P2–P4–P3 88.27(5), P3–P5–P1 81.58(4), P3–P5–P2 88.72(5), P1–P5–P2 83.52(4), N1–P3–P4 116.2(1), N1–P3–P5 112.2(1), P6–N1–P3 121.4(2), N2–P6–N1 110.6(2), P1–P4–P5–P2 118.59(6), P1–P4–P5–P3 –113.97(6), P2–P4–P5–P3 127.44(6), P3–N1–P6–N2 –167.9(2).

knowledge, compound **16** is the first example of a bicyclo[1.1.1]pentaphosphane derivative.

In our attempts to fully characterize compound **16**, it transpired that this species was rather unstable and only of intermediary nature. Several NMR experiments were run using isolated crystals of compound **16** as well as the reaction mixture of **2** and $\text{Cp}_2\text{Ti}(\text{BTMSA})$ (Figure S13). All experiments eventually indicated the formation of a similar product mixture as observed for the reduction of **2** with Mg. Hence, the formation of $\text{Mes}^*\text{P}_4\text{Mes}^*$ can be rationalized by formal cleavage of the P3–P4 and P3–P5 bonds in compound **16**.

Despite its inherent instability, compound **16** could be identified by ^{31}P NMR spectroscopy in a solution that was freshly prepared from isolated crystals. The six phosphorus atoms displayed an ABGM_2X spin system (Figure 5), with typical NMR shifts for the Mes^* -substituted P atoms (–26.0, –21.0 ppm)^[29] and a downfield-shifted X part corresponding to the P atom involved in the NP double bond (281.3 ppm). The experimental shifts and coupling constants, which were extracted from the spectrum by line-shape fitting, correspond very well to calculated NMR data (Table 2).

Natural bond orbital (NBO) and natural localized molecular orbital (NLMO) analysis^[62,63] of **16** revealed that all P atoms of the P_5 scaffold are connected by localized σ -type bonds, and that each atom possesses one LP that is mainly localized in an s orbital (s-character: 65–69%). The Wiberg bond indices of the PP bonds range from 0.90 to 0.95, indicating typical PP single bonds in agreement with experimental structural data. The exocyclic NPN scaffold comprises an NP double bond (N2=P6) and a p-type LP at N1, which interacts slightly with the anti-bonding π^* orbital (donor–acceptor energy $E^{(2)} = 106.6 \text{ kJ mol}^{-1}$). Again, these findings are in line with the experimental structure.

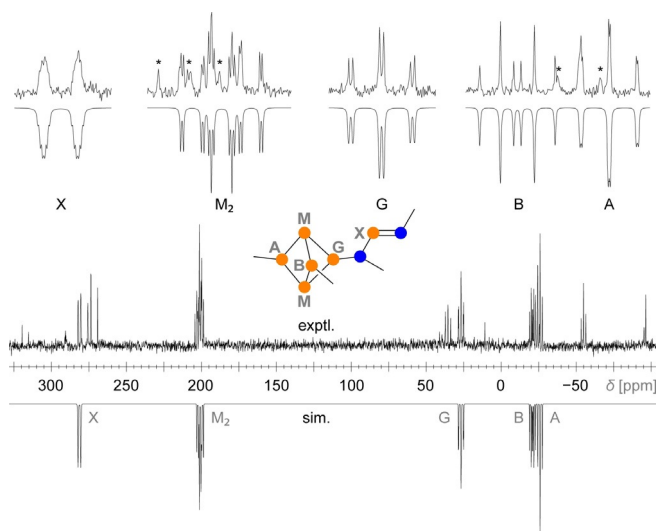
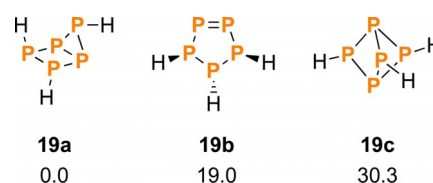


Figure 5. ^{31}P NMR spectrum of a solution containing cage compound **16**. The experimental spectrum (up) shows some impurities due to the instability of **16**. The simulated spectrum (down) was fitted to the most intense signals. A detailed view of all signals is presented at the top (lines caused by impurities are indicated by an asterisk).

Table 2. Experimental ^{31}P NMR data of **16** (ABGM_2X spin system). Calculated values (PBE0-D3/def2-TZVP, cf. SI) are given in brackets.

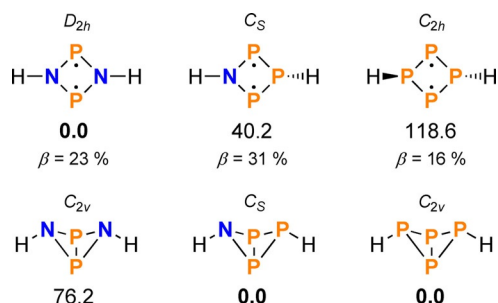
	δ [ppm]	J [Hz]			
		A	B	G	M
A	–25.0 (–19.0)				
B	–21.0 (–26.6)	–4 (–14)			
G	26.7 (29.9)	–6 (–22)	–3 (–9)		
M_2	200.7 (189.9)	–185 (–132)	–136 (–83)	–202 (–160)	
X	281.3 (283.7)	–14 (–15)	+224 (+288)	–28 (–36)	+19 (+47)

The stability of different P_5H_n ($n=0-7$) structures has been investigated theoretically and experimentally in a number of publications.^[64–71] Still, the bicyclo[1.1.1]pentaphosphane motif was considered only in a single publication, which identified the minimum energy structure of P_5H_3 as bicyclo[2.1.0]pentaphosphane (**19a**).^[68] This is in agreement with our own results, which show that bicyclo[1.1.1]pentaphosphane (**19c**) is in fact the least favoured isomer of those previously discussed in the literature (Scheme 15, see also p. S40).



Scheme 15. Different isomers of P_5H_3 and their relative Gibbs energies (ΔG° in kJ mol^{-1} , DLPNO-CCSD(T)/def2-TZVP//PBE0-D3/def2-TZVP).

Since we did not find clear experimental evidence whether the reduction of the NP_3 ring system **2** led to intermediary formation of the biradical (**17**) or bicyclic isomer (**18**) of $\text{Mes}^*\text{NP}_3\text{Mes}^*$ (cf. Supporting Information, pp. S35f and Scheme 16 for $\text{R}=\text{H}$), DFT and ab-initio calculations were performed to compare both isomers (for details on computations, please refer to the Supporting Information). As already indicated, the bicyclic structure **18** is energetically slightly favoured ($\Delta G^\circ = 14.2 \text{ kJ mol}^{-1}$). When disregarding effects of the bulky substituents, that is, using H_2NP_3 as a model compound, the difference in energy between both isomers is somewhat more pronounced ($\Delta G^\circ = 40.2 \text{ kJ mol}^{-1}$, Scheme 16). By comparison, the energetic difference between biradical and bicyclic structure of H_2P_4 amounts to $118.6 \text{ kJ mol}^{-1}$, rendering the hypothetical H_2P_4 biradical very unstable. In contrast, the $\text{H}_2\text{N}_2\text{P}_2$ biradical is substantially more stable than the bicyclic structure ($\Delta G^\circ = -76.2 \text{ kJ mol}^{-1}$), in agreement with earlier considerations and experimental observations.^[26,46]



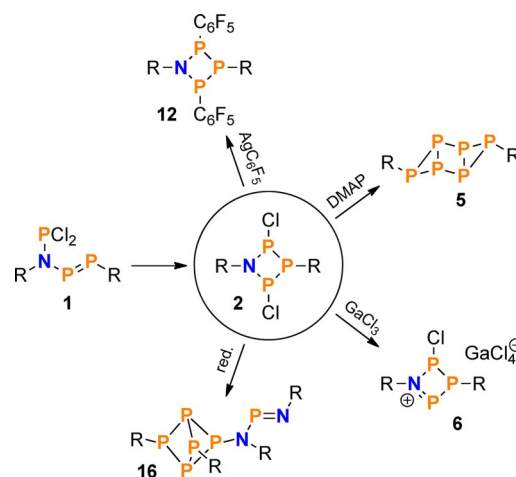
Scheme 16. Comparison of N_2P_2 , NP_3 and P_4 ring systems with respect to the relative stabilities of biradical and bicyclic isomers (ΔG° in kJ mol^{-1} , DLPNO-CCSD(T)/def2-TZVP//PBE-D3/def2-SVP).

The biradical character of H_2NP_3 was computed to be 31%, which is slightly larger than the biradical character of its N_2P_2 congener (23%; cf. $[\text{P}(\mu\text{-Nter})]_2$ (**14**): 27%).^[72] The predicted biradical character of the P_4 species is still smaller (16%), which can be attributed to a different through-bond interaction in the absence of a N atom.^[73,74] Overall, the biradical character of all three species is moderate and compares with other pnictogen-based biradicals.^[75–79]

Conclusion

In conclusion, it was shown that the chemistry of the NP_3 ring system **2** systematically expands the known chemistry of congeneric N_2P_2 and P_4 ring systems. Some similarities with these known compounds notwithstanding, we could observe some unexpected reaction behaviour, such as the formation of a bicyclo[1.1.1]pentaphosphane derivative (**16**) or the formation of products with formal $[\text{NP}]_n$ and $[\text{PP}]_n$ composition due to formal cycloreversion of the NP_3 ring system (e.g. $\text{Mes}^*\text{P}_6\text{Mes}^*$ (**5**), Mes^*NPCl , or $(Z)\text{-Mes}^*\text{PPC}_6\text{F}_5$; cf. Scheme 17).

In particular, it was demonstrated that chloride abstraction from **2** using a Lewis acid such as GaCl_3 resulted in the formation of a highly labile azatriphosphenium salt (**6**). Substitution



Scheme 17. Summarized reactivity of the NP_3 ring system **2**.

of the Cl atoms with C_6F_5 , on the other hand, gave a rather stable NP_3 ring system (**12**), which underwent partial cycloreversion in solution to yield a diphosphene and an iminophosphane. Most intriguingly, the reduction of **2** afforded a bicyclo[1.1.1]pentaphosphane (**16**), an as yet uninvestigated substance class.

Comprehensive theoretical studies were performed to understand the differences and similarities between N_2P_2 , NP_3 and P_4 ring systems. One main factor that governs the stability of the products is the electronic structure of the lone pairs of electrons at N versus P: The p-type lone pair at N can easily delocalize into the ring system, resulting in resonance stabilization of highly reactive species, whereas the s-type lone pair at P is rather unsuited for this kind of interaction. Moreover, the ring strain at N versus P plays a role in the stability of different ring systems, as previously detailed elsewhere.^[45,46]

In consequence, N_2P_2 derivatives tend to form planar ring systems (often involving electron delocalization), while P_4 systems may stabilize themselves by intramolecular bond formation (bicyclic structures). The investigated reactivity of the NP_3 ring system **2** implies that, in case none of the former types of stabilization predominate, cycloreversion becomes important as an alternative pathway of energy gain. This is often associated with a mixture of products, rendering the isolation of pure substances a challenge.

Experimental Section

All manipulations were carried out under oxygen- and moisture-free conditions in an inert atmosphere of argon, using standard Schlenk or Drybox techniques. For detailed synthetic protocols, analytic data and experimental spectra please refer to the Supporting Information.

CCDC 1939289, 1939290, 1939291, 1939292, 1939293, 1939294 and 1939295 contain the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre.

Computations were performed using the programs Gaussian09^[80] and Orca 4.1.1.^[81] Structure optimizations employed the pure den-

sity functional PBE or hybrid functional PBE0,^[82–84] in conjunction with Grimme's dispersion correction D3(BJ).^[85,86] For more accurate single-point energies, the DLPNO-CCSD(T)^[87–89] method was applied. All calculations used the basis sets def2-SVP or def2-TZVP.^[90] Detailed information on all calculations is given in the Supporting Information.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: biradicals · computational chemistry · phosphorus · PN chemistry · ring systems

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