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The First Synthesis of the Sterically Encumbered Adamantoid Phosphazane $P_4(N^tBu)_6$: Enabled by Mechanochemistry

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Abstract: *All reported attempts to synthesize the tert-butyl-substituted adamantoid phosph(III)azane $P_4(N^tBu)_6$ have failed, leading to the classification of this molecule as inaccessible and a literature example of steric control in chemistry of phosphorus-nitrogen compounds. We now demonstrate that this structure is readily accessible by a solvent-free mechanochemical milling approach, highlighting the importance of mechanochemical reaction environments in evaluating chemical reactivity.*

Carbon-based covalent structures have been extensively studied and developed across a myriad of applications involving small molecules as well as polymeric and extended frameworks.[1] In contrast, the chemistry of covalent structures based on non-carbon backbones is much less advanced, with the exception of specific compound families that are based on strong covalent bonds of the Si–O (silicate minerals, zeolites, silicone polymers), P–O (e.g., phosphate ceramics and biologically occurring phosphates), or P–N (e.g., phosphazane polymers) type.[2] However, most non-carbon-based covalent arrangements are labile and highly air- and moisture-sensitive, making their synthesis challenging. Hence the design and synthesis of complex inorganic covalent structures still remains an underdeveloped area in comparison to their organic counterparts.[3]

Since the isolation of the first phosphorus–nitrogen (PN) heterocycle,[4] there has been growing interest in such systems, and especially in cyclophosphazanes based on a saturated PN backbone. The importance of cyclophosphazanes arises from their structural versatility,[5–10] with applications as multidentate ligands,[11] (asymmetric)[12] catalysts for organic synthesis,[13] and antitumor drugs.[14] The structure of the PN backbone in cyclophosph(III)azanes is controlled by steric and stoichiometric factors. A classic illustration of strict steric control is the $[XP(\mu\text{-}NR)]_2$ dimer (**I**; Figure 1 a) observed for sterically demanding groups (e.g., R = ^{t}Bu), whereas trimers

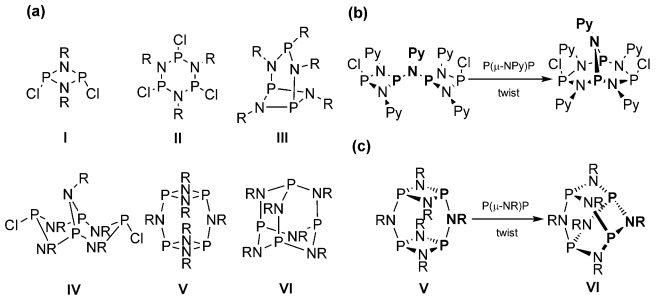

Figure 1. a) Selected PN backbones. b, c) The twist isomerization mechanism for cyclophosphazanes.[17].

$[XP(\mu\text{-}NR)]_3$ and larger structures are obtained with smaller substituents (e.g., R = Me, Et; Figure 1 a, **II**–**V**).[6,15] The steric demand of the nitrogen substituent is thought to control the stability and accessibility of different cyclophosph(III)azane isomers, which can interconvert under suitable conditions,[16] for example by the twist mechanism found in the formation of the type **IV** phosphazane $[\{ClP(\mu\text{-}Npy)_2\}_2\{P_2(\mu\text{-}Npy)\}]$ (Figure 1 b).[17] The twist mechanism was also proposed for the conversion of type **V** macrocycles, $[\{P(\mu\text{-}NR)\}_2(\mu\text{-}NR)]_2$, into the thermodynamically preferred type **VI** adamantoid isomer $P_4(NR)_6$ (Figure 1 c).[17] For the isopropyl-substituted macrocycle $[\{P(\mu\text{-}N^iPr)_2\}_2(\mu\text{-}N^iPr)]_2$ (**1**), conversion into the adamantoid isomer **2** is achieved by prolonged heating in a sealed tube (Scheme 1).[18] However, over the past two decades, all reported attempts to convert the *tert*-butyl-substituted double-decker macrocycle $[\{P(\mu\text{-}N^tBu)\}_2(\mu\text{-}N^tBu)]_2$ (**3**) into its adamantoid isomer (**4**) have failed (Scheme 1).[19]

Furthermore, whereas the direct synthesis of adamantoid $P_4(NR)_6$ backbones by reaction of PCl_3 with RNH_2 was successful for less sterically hindered amines (i.e., R = Me, Et, ^{i}Pr), it failed for bulky ^{t}BuNH$_2$. These results led to the conclusion that the type **V** macrocyclic backbone is the more stable one in the presence of bulky ^{t}Bu groups.[20] Thus **4** has been classified as inaccessible on steric grounds and is usually cited as an example of steric control in PN compounds.[17,21]

Herein, we demonstrate that this thus far elusive molecular structure is readily accessible by adopting a mechanochemical approach based on ball milling.[22] Our study indicates that previous inability to access this molecule is

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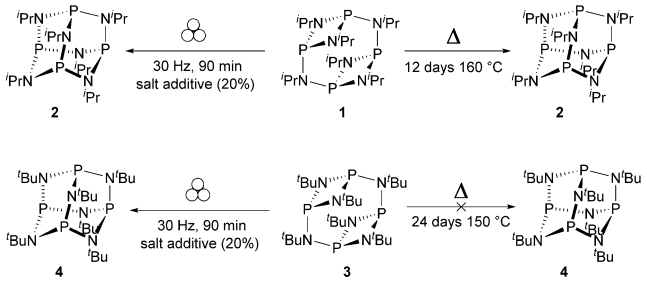

Scheme 1. The isodesmic isomerization of $[\{P(\mu\text{-}NR)\}_2(\mu\text{-}NR)]_2$ (**V**) into $P_4(NR)_6$ (**VI**) by ball milling (left) has thus far been difficult (for **2**) or impossible (for **4**) to achieve by solution methods (right). The symbol for mechanical milling was proposed by Hanusa et al.[26a]

not due to steric effects, but to inherent limitations of chemical reactivity in solution.

Mechanochemistry has emerged as an excellent solvent-free and atom-efficient alternative to conventional solution-based chemistry,[23] providing access to novel organic transformations and the synthesis of otherwise inaccessible molecules.[24,25] However, mechanochemistry has been hardly explored in the context of non-carbon backbones and organometallic compounds.[26] We now demonstrate how the application of mechanochemistry resolves a long-standing challenge of cyclophosphazane chemistry by enabling the formation of adamantoid $P_4(N^tBu)_6$ (**4**) by isodesmic isomerization of its sterically encumbered cyclic dimeric phosph-(III)azane counterpart **3** (Scheme 1).[21]

Our first goal was the conversion of **1** into its adamantoid isomer **2** by ball milling. Previously, Wolmerhäser and co-workers had reported that this rearrangement occurs only upon prolonged heating at high temperature (12 days at 160 °C).[18] An attempt to conduct the isomerization of **1** by milling for 90 min in a Retsch MM400 mixer mill operating at 30 Hz loaded with a 10 mm stainless steel ball (4 g) was unsuccessful, as evidenced by the $^{31}P\{^1H\}$ NMR spectrum of the milled material recorded in THF. Next, we explored modified mechanochemical approaches, by milling in the presence of a small amount of a liquid (liquid-assisted grinding, LAG) or salt additive, which has previously shown to enhance and direct mechanochemical transformations.[27] Milling of **1** in the presence of toluene or THF (100 μL per 100 mg of solid reactant, corresponding to an η parameter[28] of 1 $\mu L\,mg^{-1}$) led to thus far unprecedented room-temperature formation of adamantoid **2**. The conversion into **2** was about 20 %, but screening a series of different liquid and solid milling additives (see the Supporting Information, Table S1) revealed that the presence of 20 wt % LiCl in the milling mixture led to almost quantitative production of **2** after 90 min milling. This is in stark contrast to the extended reaction times and harsh reaction conditions required for the solution reaction (see above).[18] The formation of **2** was confirmed by ^1H, ^{13}C, and ^{31}P NMR spectroscopy in solution and in the solid state (see the Supporting Information). The obtained spectroscopic data are fully consistent with the literature,[18,20] and the formation of **2** was fully ascertained by single-crystal X-ray diffraction after recrystallization from CH_3CN (Figure 3).

Next, we also explored the milling of **3** in the presence of additives (see the Supporting Information). Similarly to the mechanochemical isomerization of **1**, milling of **3** in the presence of 20 wt % LiCl readily and quantitatively yielded **4**, which was previously thought to be inaccessible, after 90 min. This is particularly remarkable considering that **3** was reported not to isomerize even after heating at 150 °C for 24 days.[19] To further evaluate the influence of standard reaction conditions on the formation of **4**, **3** was heated at reflux in various solvents (e.g., ether, hexane, THF, toluene, and DMF) with identical amounts of the salt additive. In all cases (with the exception of DMF, where **3** decomposed upon prolonged heating), the formation of **4** was not observed in the $^{31}P\{^1H\}$ NMR spectrum of the sample even after extended reaction times, supporting the view that this adamantoid structure is not accessible by solution methods.

After recrystallization from toluene, **4** was characterized by ^1H, ^{13}C, and ^{31}P NMR spectroscopy in solution, as well as by powder X-ray diffraction and solid-state NMR spectroscopy (see the Supporting Information). The $^{31}P\{^1H\}$ NMR spectrum for **4** at room temperature exhibits a singlet resonance at $\delta = 54.47$ ppm (Figure 2), which is comparable to that found for its ^{i}Pr counterpart ($\delta = 84.41$ ppm, but $\delta =$

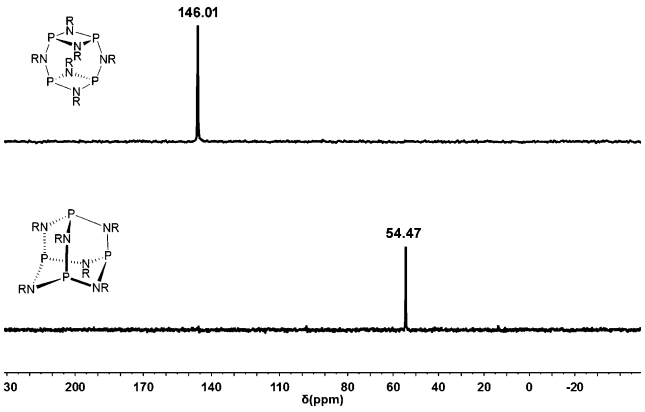

Figure 2. $^{31}P\{^1H\}$ NMR spectra of $[\{P(\mu\text{-}N^tBu)\}_2(\mu\text{-}N^tBu)]_2$ (**3**; top) and $P_4(N^tBu)_6$ (**4**; bottom) in C_6D_6. Further NMR spectra for compounds **1**–**4** are given in the Supporting Information.

117.2 ppm in **3**). The ^{13}C NMR spectrum shows two single resonances at $\delta = 59.29$ and 31.38 ppm ($\delta = 59.83$, 55.12, 34.72, and 29.95 ppm in **3**; see the Supporting Information). In contrast to its precursor **3**, the room-temperature ^1H NMR spectrum of **4** shows only one single resonance at $\delta =$ 1.51 ppm (1.57 and 1.53 ppm in **3**; see the Supporting Information), which is diagnostic of isomerization to an adamantoid structure. Low-temperature single-crystal structures of **2** and **4**, which were obtained from diffraction studies of crystals grown from CH_3CN and toluene, respectively, are in agreement with the initial spectroscopic analyses (Figure 3). The average P–N bond distance in **4** (1.72 Å) is

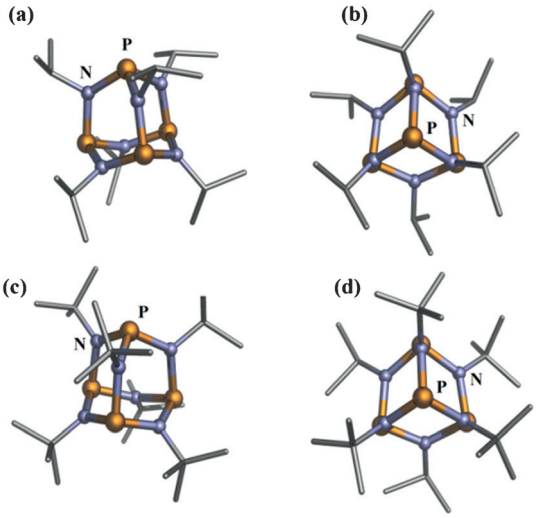

Figure 3. Single-crystal structures of **2** (a, b) and **4** (c, d). For selected bond lengths and angles, see the Supporting Information. Hydrogen atoms are omitted for clarity. C gray, N blue, P orange.[34]

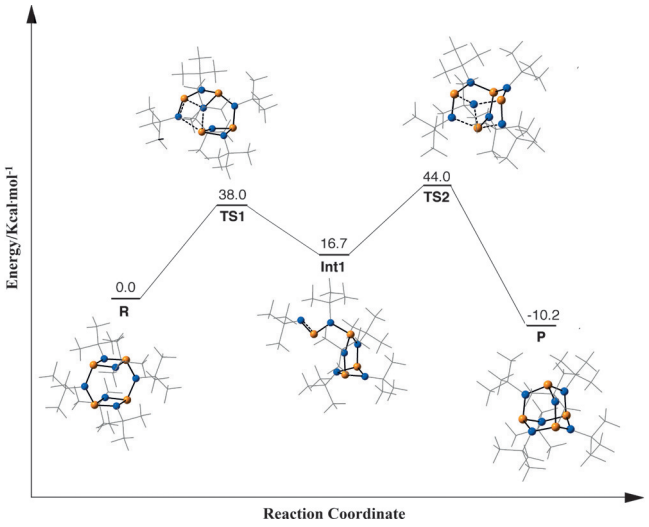

Figure 4. Energy diagram (in kcal mol^{-1}) for the isodesmic isomerization of **3**→**4**, calculated at the B3LYP/B2//B3LYP/B1 + ZPE level of theory. C gray, N blue, P orange.

comparable to that in analogous compounds containing less sterically demanding N substituents (1.69 Å and 1.71 Å in $P_4(NMe)_6$ and $P_4(NEt)_6$, respectively), which supports our view that the previous inability to synthesize **4** was not due to steric constrains.[8a,29]

The efficiency of the mechanochemical isomerization appears to be strongly dependent on the amount of LiCl present in the reaction mixture: At 10 wt %, the reaction did not take place within 90 min of milling, whereas at 30 wt %, the conversion was not quantitative. The lack of reactivity at a lower LiCl loading may be explained by the low salt concentration, while the reduction in reactivity upon increasing the amount of LiCl above 20 % is tentatively explained by dilution effects and less efficient mechanical impact on the phosphazane reactant. As the formation of **4** is surprising and in contrast to the established understanding of cyclophosphazane chemistry, we decided to confirm the viability of the isodesmic **3**→**4** isomerization by single-molecule density functional theory (DFT) calculations (see the Supporting Information). In contrast to our initial expectation that such an isomerization should proceed through the twist mechanism,[17] the computational study suggests a stepwise mechanism in which the first step entails the formation of one P–N bond while two others are cleaved, passing through transition state **TS1** (Figure 4). The resulting postulated intermediate **Int1** adopts a bicyclic [3,1,1] structure resembling a type **III** backbone (Figure 1). Although we have thus far not been able to experimentally confirm the existence of **Int1**, such cyclophosph(III)azane structures have been previously reported, for example, for R = Cl, N_3, and $N(SiMe_3)_2$,[30] supporting the plausibility of the proposed mechanism. In the next step, the reaction passes through transition state **TS2** to form the final adamantoid structure. The overall reaction is exothermic (ca. 43 kJ mol^{-1}), but involves very high energy barriers (ca. 160 and 114 kJ mol^{-1} for **TS1** and **TS2**, respectively; Figure 4). Such high energy barriers provide a potential explanation for why this molecule had remained inaccessible for such a long time. The calculated free energies, ΔG, for **Int1** and compound **4** relative to the reactant are approximately 62 and −44.8 kJ mol^{-1}, respectively. Calculations performed on the reaction in the presence of lithium chloride suggest that the salt additive does not lower the activation barrier (see the Supporting Information).

In summary, we have described the first application of mechanochemistry for the transformation of non-carbon covalent backbones. The application of ball milling enabled the rapid room-temperature synthesis of the adamantoid isopropyl-substituted cyclophosphazane **2**, a molecule that was previously accessible only by extended harsh heating of the starting bicyclic isomer. Most importantly, mechanochemistry permitted the synthesis of the *tert*-butyl-substituted adamantoid cyclophosphazane **4** for the first time, which had thus far been considered as a textbook example of a sterically inaccessible molecule in main-group chemistry. It is tempting to rationalize the unprecedented formation of **4** by milling in terms of the effect of mechanical shear on the electronic structure of the reactants.[31] However, such effects of shear on chemical reactivity have thus far been reported only for polymers and extended frameworks, wherein pulling on a molecular chain can cause a mechanical effect on a reactive (mechanophore) site.[32] For materials based on small molecules, milling is more likely to cause the formation of short-lived "hot spots" or a high-energy amorphous phase that can serve as a non-conventional, continuously agitated reaction environment.[27,33] We believe that the herein presented formation of a previously inaccessible molecule is a breakthrough in main-group chemistry. Our results illustrate the transformative potential that switching to a solvent-free or solvent-reduced mechanochemical environment can have on established chemical syntheses.

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[34] CCDC 1417218 (**2**) and 1035873 (**4**) 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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