

# P<sub>4</sub> Activation by Main Group Elements and Compounds

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Manfred Scheer studied chemistry at the University of Halle-Wittenberg (Germany). Here he received his Diploma in 1980 and his Dr. rer. nat. degree in 1983, both in organometallic tin(II) chemistry (with Alfred Tzschach and Klaus Jurkschat). After postdoctoral research on solid state chemistry at the Institute of Inorganic Chemistry of the Russian Academy of Sciences in Novosibirsk and on main group centered multinuclear metal-promoted catalysis at the Max-Planck-Institute für Kohlenforschung in Mülheim/Ruhr with Gerhard Wilke, he finished his habilitation in the field of phosphorus chemistry in Halle/S. in 1992. Promoted by a Feodor Lynen Fellowship of the Alexander von Humboldt Foundation, he researched as guest professor with Malcolm Chisholm at Indiana University, Bloomington, IN, in 1992/93. In 1993 he returned to Germany at the Institute of Inorganic Chemistry of Karlsruhe as a Heisenberg Fellow of the Deutsche Forschungsgemeinschaft, where he was appointed as Associated Professor of Chemistry (C3) in 1996. In 2004 he accepted the chair of Inorganic Chemistry at the University of Regensburg (Germany). His research interests include the synthesis and investigation of reactivity patterns of unsubstituted main group element ligands with a focus on the heavier group 15 elements as well as the stabilization and reactivity of main group compounds consisting of combinations of different elements. The chemistry of highly reactive molecules such as P<sub>4</sub>, As<sub>4</sub>, or compounds containing transition metal group 15 element multiple bonds is of further interest.

phorus directly to the desired industrial inorganic and organic phosphorus containing products. These have been the goals of intensive industrial as well as academic research in the mentioned period of the 1970s and 1980s by using main group elements and compounds to transfer P<sub>4</sub> directly to useful products. However, the low selectivity and the problems in the workup of the reaction mixtures usually obtained make these new processes noncompetitive with established industrial procedures. Moreover, the discovery in the late 1970s and mid-1980s that transition metal complexes can coordinate,<sup>2</sup> activate,<sup>3</sup> and transform<sup>4</sup> white phosphorus led to the possibility of transition metal mediated activation and transformation of white phosphorus. This period of intensive research of P<sub>4</sub> activation by transition metal complexes started in the mid-1980s and is still being developed.<sup>5</sup> Here, the main steps of the gradual activation of P<sub>4</sub> phosphorus are, in principle, understood.<sup>6</sup> Although the transition metal-mediated activation of white phosphorus

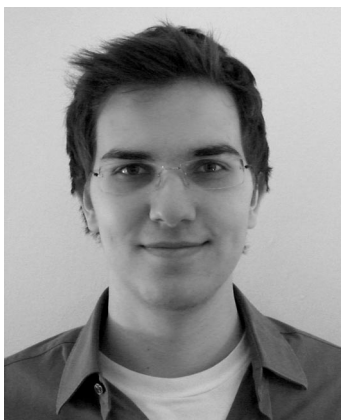
## 1. Introduction

The activation of white phosphorus by main group elements and compounds is an established field of chemistry which had its initial high impact back in the 1970s and 1980s, when numerous groups worldwide used P<sub>4</sub> as starting material to generate organophosphorus compounds. Its use is based on the availability of white phosphorus as a first industrial product after transformation from phosphate minerals and on a great industrial relevance for subsequent inorganic and organophosphorus products.<sup>1</sup> Here lies the key role of white phosphorus, since most industrial processes in the past and in the present are based on its further chlorination or oxychlorination to PCl<sub>3</sub>, PCl<sub>5</sub>, and POCl<sub>3</sub>. Using HCl or salt elimination reactions, these compounds react to produce subsequent products such as phosphoric and phosphonic acids and esters as well as organophosphorus derivatives of tri- and pentavalent phosphorus. To avoid these necessary steps needed so far and to achieve the criteria of more sustainable and environmentally friendly processes, extreme efforts have been directed to transfer white phos-

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Andreas Seitz was born in Landshut, Germany, in 1989. In October 2008 he started his undergraduate studies in chemistry at the University Regensburg (Germany), where he joined Prof. Dr. M. Scheer's chair as a student assistant in October 2009.

has achieved impressive progress over the years, which is documented in two actual review articles in this series,<sup>7</sup> the most unsolved step in this area is the combination of activated transition metal phosphorus species with organic substrates to yield organophosphorus products. Moreover, the target of *catalytic* functionalization of P<sub>4</sub> phosphorus is still far from being solved. Parallel to the ongoing research of transition metal-mediated activation of P<sub>4</sub> phosphorus during the last five years, a renaissance of activation and degradation of white phosphorus by main group compounds is noticed.<sup>8</sup> These activities are dominated by metal-free P<sub>4</sub> degradation in the Bertrand group by NHC and CAAC reagents and can be seen in line with already earlier reported activation of P<sub>4</sub> phosphorus by carbene analogues of group 13 and heavier group 14 elements. Also, cationic phosphonium compounds, which are also carbene-like species, have been successfully applied to insert into P–P bonds of white phosphorus (details are discussed in section 4). According to these decisive developments, this review intends to provide a comprehensive view of the current stage of activation and

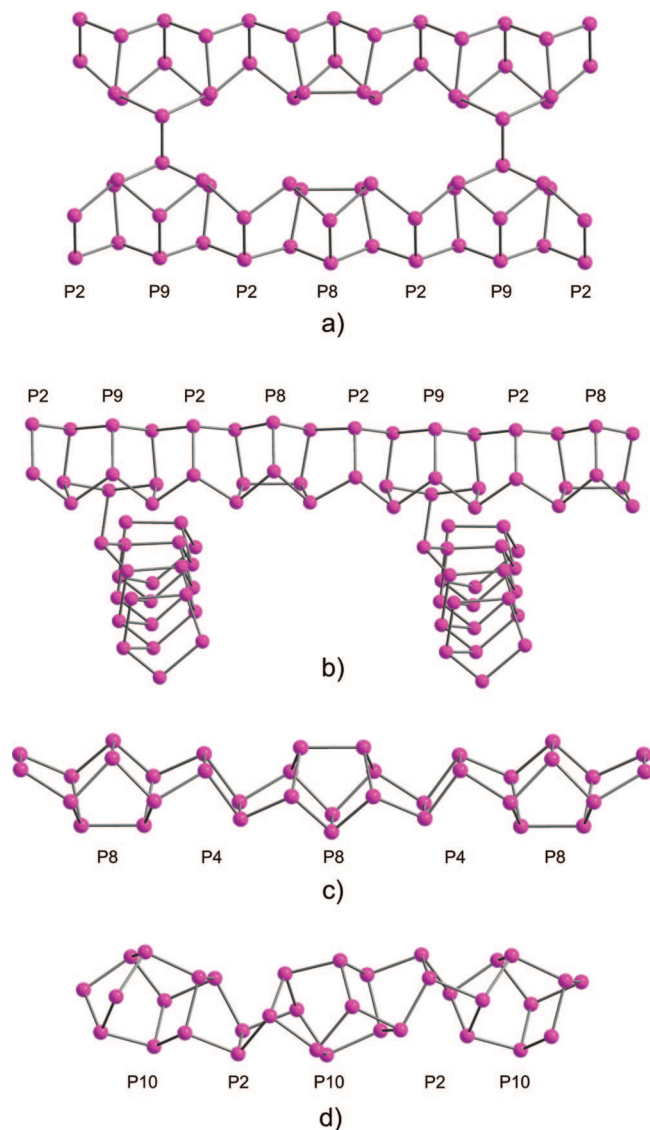
degradation of white phosphorus by main group elements and compounds. Yet, in the face of the large number of early contributions in this area reviewed over the years by some articles on organophosphorus compounds derived from P<sub>4</sub>,<sup>9</sup> this article is dedicated to the development of the field of P<sub>n</sub> rich compounds ( $n > 4$ ) and also to the recent findings of P<sub>4</sub> activation and degradation. By trying to draw general lines and trends, the project is faced with the difficulty of having incomplete experimental proofs and understanding of the single steps of the P<sub>4</sub> activation by main group element compounds. In view of large amounts of individual results and the lack of detailed mechanistic knowledge, this review provides insight into the current stage of research. Furthermore, we want to stimulate the inorganic, organic, catalytic, and material science oriented chemical community to draw much more attention to the field of P<sub>4</sub> activation by main group compounds to one day accomplish direct P<sub>4</sub> based modern chemical manufacturing.

## 2. The Stability of P<sub>4</sub> Phosphorus with Respect to Its Allotropes and Neutral Polyphosphorus Species

### 2.1. Allotropic Modifications of Phosphorus

Three basic allotropic modifications of elemental phosphorus exist in general chemistry textbooks: white, red, and black phosphorus. The structure of the thermodynamically most stable form of black phosphorus is known as well as the one of white tetrahedral P<sub>4</sub> phosphorus.<sup>10</sup> At ambient temperature and pressure, black phosphorus reveals an orthorhombic structure,<sup>11</sup> whereas, by increasing pressure, the structure changes first into a rhombohedral form and then into a cubic form.<sup>12</sup> At room temperature, white phosphorus is a waxy material which is difficult to obtain as single crystals. In spite of this, Simon et al. elucidated the  $\beta$ -P<sub>4</sub><sup>13a,b</sup> and  $\gamma$ -P<sub>4</sub><sup>13c</sup> modification by single crystal X-ray and X-ray powder diffraction, respectively.<sup>14</sup> Here the point of interest for a preparative chemist is the benchmark of a P–P single bond length, which is usually referred to as the one of the gaseous P<sub>4</sub> determined by electron diffraction at 470 K to be 2.21(2) Å.<sup>15</sup> An analysis of the vibration–rotation Raman spectrum yields 2.2228(5) Å,<sup>16</sup> and in  $\beta$ -P<sub>4</sub>, P–P distances of 2.199–2.212 Å<sup>13</sup> are found by applying a rigid body libration correction. However, according to quantum chemical calculations, a value of 2.194 Å is appropriate<sup>17</sup> (for the P<sub>2</sub> moiety, 1.898 Å<sup>18</sup>). Owing to the experimental uncertainties, the use of the calculated values is recommended for reference purposes.

When white phosphorus is heated or irradiated by UV light, it is transformed to amorphous red phosphorus. The structure of the red phosphorus is regarded to be a polymeric network of different building units. Commercially available red amorphous phosphorus is entitled as “type I”. By further annealing, four crystalline phases are formed, labeled as types II, III, IV, and V red phosphorus, characterized by X-ray powder diffraction.<sup>19</sup> Among these phases, in 1966 the red phosphorus V form was structurally characterized by X-ray diffraction by Thurn and Krebs,<sup>20</sup> which was identified to be the so-called violet or Hittorf's phosphorus, that Hittorf described earlier in 1865.<sup>21</sup> Recently, Ruck et al. were able to characterize a second form by single crystal X-ray diffraction, the red phosphorus IV modification as fibrous phosphorus.<sup>22,14</sup>



**Figure 1.** Phosphorus strands of  $\frac{1}{\infty}\{[P_2[P_8]P_2[P_9]]\}$  in (a) fibrous phosphorus, (b) violet phosphorus, (c)  $\frac{1}{\infty}\{[P_4[P_8]]\}$ , and (d)  $\frac{1}{\infty}\{[P_2[P_{10}]]\}$ . For the notations P2, P4, P8, P9, and P10, cf. ref 23.

As shown in Figure 1a and b, in these two allotropes, P<sub>8</sub> cuneane-type units are connected with P<sub>9</sub> moieties by a P<sub>2</sub> linker. According to the nomenclature developed by Häser et al.,<sup>23</sup> both types are described as  $\frac{1}{\infty}\{[P_2[P_8]P_2[P_9]]\}$  strands, which are linked crosswise with one another via P<sub>9</sub> units (Hittorf's phosphorus) or parallel under formation of double tubes (fibrous phosphorus). Corresponding to theoretical calculations, both forms are isoenergetic cluster equilibrium structures. Furthermore, by polymerization of elemental phosphorus in a CuI matrix, three different polymers, (CuI)<sub>8</sub>P<sub>12</sub>,<sup>24</sup> (CuI)<sub>2</sub>P<sub>14</sub>,<sup>25a</sup> and (CuI)<sub>3</sub>P<sub>12</sub>,<sup>25b</sup> were obtained, the latter two of which were isolated after removal of CuI by an aqueous KCN solution, yielding nanorod-like polymers  $\frac{1}{\infty}\{[P_4[P_8]]\}$  and  $\frac{1}{\infty}\{[P_2[P_{10}]]\}$  as new allotropes of phosphorus.<sup>26</sup> Recently, polycrystalline phosphorus nanorods were synthesized from P<sub>4</sub> phosphorus catalyzed by Bi nanoparticles which reveal similarities to the red phosphorus II form.<sup>27</sup> Moreover, a nanocomposite of red phosphorus with organophosphorus compounds was obtained by radiation-induced ( $\gamma$  radiation of <sup>60</sup>Co) polymerization of white phosphorus in benzene at ambient temperature.<sup>28</sup> Furthermore, by neutralization–reionization (NR) mass spectrom-

etry, a benzvalene-like neutral P<sub>6</sub> molecule is proven to exist in the gas phase.<sup>29</sup>

Coming back to the phosphorus type I modification of red phosphorus, Häser et al. employed *ab initio* calculations (SCF/SVP level) to calculate energies (relative equilibrium energy given in kJ mol<sup>-1</sup> (P<sub>4</sub>)), bond lengths, and angles of violet phosphorus and others at a time when polyphosphorus strands and species were unknown.<sup>23</sup> The agreement with the experimentally determined values for Hittorf's phosphorus is so convincing that it is expected that such calculations of analogous structures of experimentally unestablished structures should also be reliable. Thus, by comparison of calculated radial distribution functions with experimentally obtained ones, Häser et al.<sup>23</sup> could show that red phosphorus most likely contains species such as  $\frac{1}{\infty}\{[P_2[P_8]P_2[P_9]]\}$  of Hittorf's phosphorus and fibrous phosphorus (the latter was unknown at that time), respectively, and  $\frac{1}{\infty}\{[P_2[P_{10}]]\}$  (all about  $E_{\text{theor}} = -61$  to  $62$  kJ mol<sup>-1</sup> (P<sub>4</sub>) relative to molecular P<sub>4</sub> phosphorus).<sup>30</sup> The latter helical strand was found afterward in the CuI matrix of (CuI)<sub>3</sub>P<sub>12</sub><sup>25b</sup> and finally in one nanorod-like allotrope of phosphorus.<sup>26</sup>

Moreover, it should be mentioned that the tetrahedral AsP<sub>3</sub> molecule was synthesized as an isolable compound by a transition metal mediated approach, and the formation of a mixture of compounds of the formulas As<sub>n</sub>P<sub>4-n</sub> ( $n = 1-3$ ) was reported.<sup>31</sup>

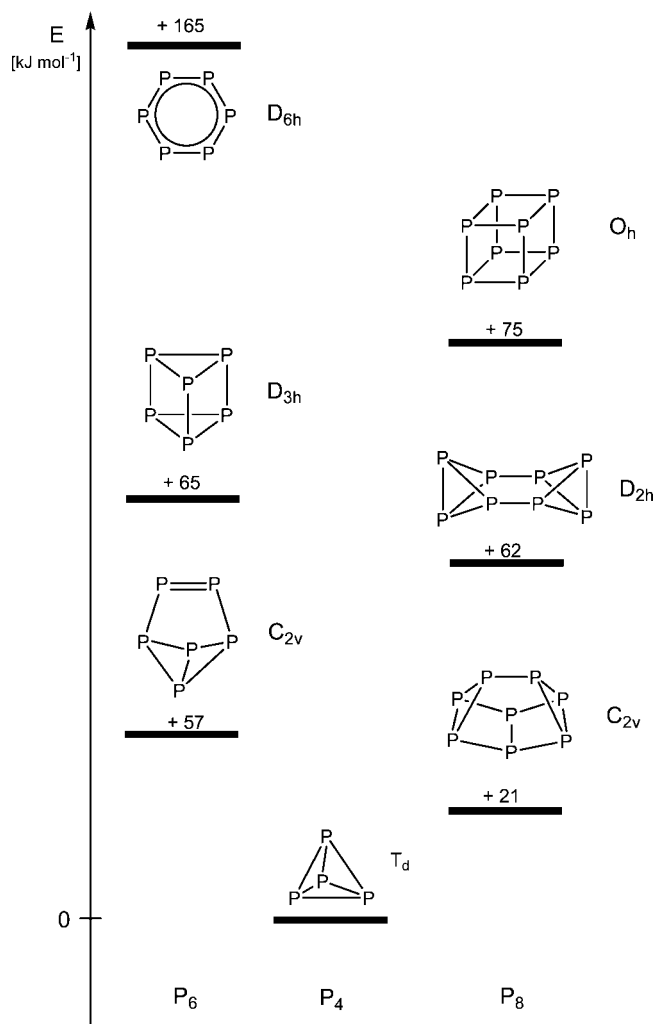
## 2.2. Stability of Neutral Polyphosphorus Species

Numerous computational studies on anionic P<sub>n</sub><sup>-</sup> clusters with  $n = 1-9$ <sup>32</sup> were done as well as for positively charged cations P<sub>(2n+1)</sub><sup>+</sup> with  $n = 3-5$ .<sup>33a</sup> In contrast, far fewer experimental facts obtained by time-of-flight mass spectrometry are known about larger polyphosphorus clusters in the form of cations P<sub>n</sub><sup>+</sup> ( $n \leq 89$ ) and anions P<sub>n</sub><sup>-</sup> ( $n \leq 49$ ) obtained by laser ablation of red phosphorus.<sup>33b,34</sup>

As already mentioned, one focus of this review is devoted to neutral polyphosphorus clusters and species, which are related in their stability to white phosphorus. From an experimental as well as theoretical point of view, the question arises whether there are neutral polyphosphorus species which are more stable than P<sub>4</sub> itself. Or, if not, what are the next stable molecules on the energy scale? Since in the case of neutral polyphosphorus species numerous calculations have been carried out with different basis sets and theoretical methods,<sup>35</sup> the comparability of these results on a consistent scale is not completely possible. Thus, in the following, even-numbered neutral polyphosphorus species are compared, whose structural parameters were calculated by *ab initio* SCF/SVP methods.<sup>23</sup> Other methods give different values of energy; however, from the relative tendencies, they show the same sequence.

Tetrahedral P<sub>4</sub> is  $-201$  kJ mol<sup>-1</sup> (P<sub>4</sub> → 2P<sub>2</sub>) more stable than the P<sub>2</sub> molecule,<sup>36</sup> which is the most unstable moiety among free P<sub>n</sub> units. Also, the aromatic cyclohexaphosphabenzene is  $20.1$  kJ mol<sup>-1</sup> more stable than three separate P<sub>2</sub> molecules.<sup>37</sup> Here the stabilization in an aromatic system is much more favorable, as is also found for anionic *cyclo*-P<sub>5</sub> moieties.<sup>38</sup> The latter is known to be a discrete species in solution,<sup>39</sup> and both are known ligands in coordination chemistry.<sup>40</sup> However, the benzene-like D<sub>6h</sub> planar hexagon is the least stable P<sub>6</sub> isomer and distorts spontaneously to nonplanar, less symmetrical 6-membered rings.<sup>41a</sup> Its aromaticity is also less pronounced than in benzene.<sup>41b-d</sup> From a thermodynamic point of view, naked polyphosphorus





**Figure 2.** Grading of the stability of P<sub>6</sub> and P<sub>8</sub> moieties in comparison to tetrahedral P<sub>4</sub> ( $1.5P_4 \rightarrow P_6$ ,  $2P_4 \rightarrow P_8$ ). Energies are given in  $\text{kJ mol}^{-1}$  (P<sub>4</sub>) relative to P<sub>4</sub> calculated at the SCF/SVP level of theory.

moieties prefer smaller bond angles, in contrast to isobal CH derivatives, which leads to different trends in stabilities.<sup>42</sup> Therefore, in the midst of P<sub>6</sub> species, the *D*<sub>3h</sub> symmetric prismane is more stable than the *D*<sub>6h</sub> symmetric *cyclo*-P<sub>6</sub>.<sup>43</sup> In addition, the benzvalene-type *C*<sub>2v</sub> symmetric molecule is even more stable (Figure 2).<sup>44</sup>

Similar tendencies are found within the P<sub>8</sub> species, for which the cubic octahedral P<sub>8</sub> was the focus of interest for a long time and thought to be an accessible species. In contrast, it is, by  $75 \text{ kJ mol}^{-1}$ , more unstable than P<sub>4</sub>,<sup>36</sup> but once it is formed, the dissociation into P<sub>4</sub> molecules from its ground state is forbidden.<sup>45a</sup> Calculations of other stable P<sub>8</sub> molecules reveal that the *C*<sub>2v</sub> symmetric cuneane is the most stable species,<sup>45b</sup> followed by a *D*<sub>2h</sub> symmetric moiety in which two tetrahedra are linked by two edges (Figure 2).<sup>44</sup> Within these smaller P<sub>n</sub> molecules (up to P<sub>10</sub> moieties), tetrahedral P<sub>4</sub> is the most stable one. Interestingly, by using SCF MO calculations at the 4-31G\* level, the P<sub>8</sub> cuneane molecule comes close in energy to  $2P_4$ ,<sup>46</sup> which was confirmed by CBS-Q calculations.<sup>47</sup> The latter calculations give evidence that at 0 K the cuneane structure is more stable ( $\Delta E^\circ = -13.8 \text{ kJ mol}^{-1}$ ) than P<sub>4</sub>, but under standard conditions still unstable for entropic reasons ( $\Delta G^\circ = +33.9 \text{ kJ mol}^{-1}$  vs  $2P_4$ ).

Beginning from P<sub>10</sub> and going to P<sub>28</sub> cages (Figure 3), there is a change in the stability relative to the tetrahedral P<sub>4</sub> molecule.<sup>23,44</sup> As shown in Figure 3, the predominantly favored P<sub>n</sub> aggregates from numerous calculated species of each composition, the species gain in energy, which are structurally more related to motives of Hittorf's phosphorus. So, if P<sub>8</sub> cuneane-like motifs are connected by P<sub>2</sub> moieties, the formed cages are energetically most favored in comparison to tetrahedral P<sub>4</sub>.

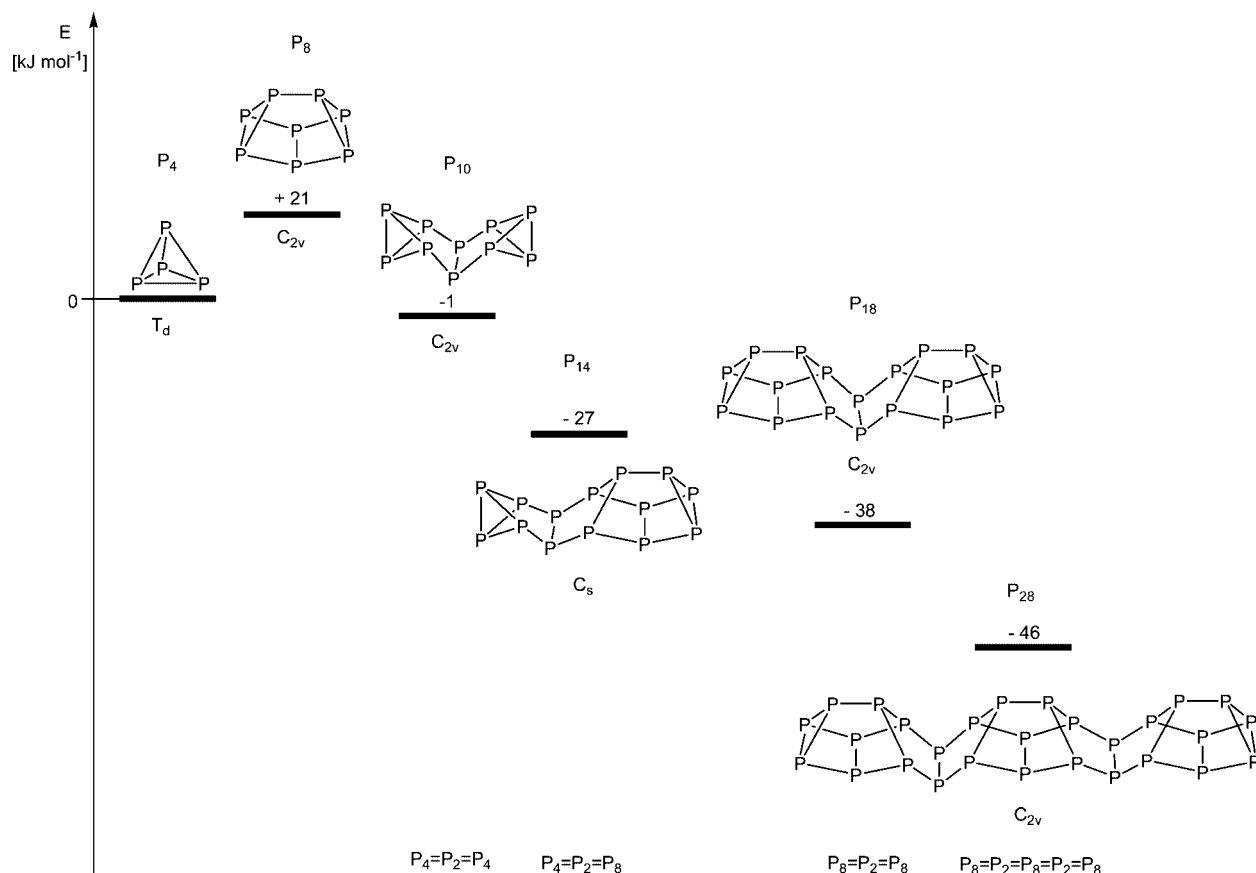
Moreover, icosahedral and ring-shaped polyphosphorus moieties have been calculated and compared in their thermodynamic stabilities to the known P<sub>n</sub> allotropes.<sup>48</sup> These calculations show the stability of icosahedral P<sub>80</sub>, P<sub>180</sub>, P<sub>320</sub>, P<sub>500</sub>, and P<sub>720</sub> species consisting of 5- and 6-membered rings is higher than that of P<sub>4</sub> phosphorus. Only the pentagon-icosahedral P<sub>20</sub> molecule is less stable. In contrast, beginning with P<sub>120</sub> up to P<sub>360</sub>, ringlike allotropes built by P<sub>8</sub> cuneane moieties and linked by P<sub>2</sub> units reveal larger stabilities than the known P<sub>n</sub> allotropes.<sup>48</sup>

### 3. General Trends of P<sub>4</sub> Phosphorus Activation

#### 3.1. General Remarks

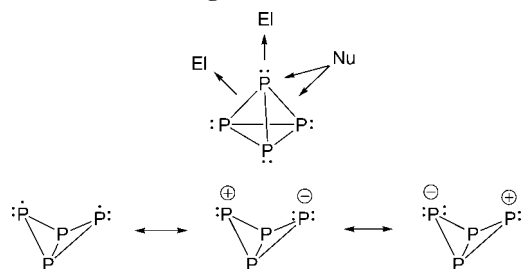
In general, the reactivity of tetrahedral P<sub>4</sub> phosphorus is attributed to the high bond strain energy.<sup>49</sup> Interestingly, newer analyses of the bonding in the P<sub>4</sub> cluster<sup>50</sup> show that in the singlet-ground-state of P<sub>4</sub> the vector linking the phosphorus nuclei and the direction of the bond critical point (BCP) is only  $\sim 5^\circ$ , which might relativize the role of bond strain. Interestingly, a kind of spherical aromaticity was discussed for P<sub>4</sub> and other inorganic cage molecules based on the nucleus-independent chemical shift (P<sub>4</sub>(*T*<sub>d</sub>)  $\delta = -52.9$ ).<sup>51</sup> The excited triplet-state of P<sub>4</sub> is  $102.3 \text{ kJ mol}^{-1}$  higher in energy in comparison to the neutral singlet-state and captures a butterfly like structure.<sup>50</sup> Oxidation of P<sub>4</sub> leads formally to P<sub>4</sub><sup>+</sup>, which is calculated to favor a *D*<sub>2h</sub> symmetric molecule with four "short" and two "long" bonds ( $1138.1 \text{ kJ mol}^{-1}$  higher than P<sub>4</sub>) in comparison to a regular tetrahedron structure of P<sub>4</sub><sup>50</sup> using the Bader topological theory.<sup>52</sup> Moreover, if P<sub>4</sub> is reduced to P<sub>4</sub><sup>-</sup>, a distorted *D*<sub>2h</sub> structure is formed which is, only by  $119.7 \text{ kJ mol}^{-1}$ , higher in energy than neutral P<sub>4</sub>. Thus, the anionic P<sub>4</sub><sup>-</sup> species seems to be decisive for P<sub>4</sub> polymerization, leading to P<sub>n</sub> allotropes which can be thermally induced, photochemically, by  $\beta^-$  radiation,<sup>53</sup> or nucleophilically. These calculations agree well with the experimental observations that P<sub>4</sub> phosphorus reacts predominantly under nucleophilic activation, revealing electrophilic reactivity. In the ground state analysis of P<sub>4</sub>, electron densities are found for the positions of electron lone pairs. These are responsible for the nucleophilic reactivity of P<sub>4</sub>. The general reactivity pattern of P<sub>4</sub> is highlighted in Scheme 1 and shows that places of predominant nucleophilicity of P<sub>4</sub> are the lone pairs at the P apexes and the filled  $\sigma$ -bond of the P–P bonds, which are, in principle, able to react with electrophiles.

However, the nucleophilicity of P<sub>4</sub> is less pronounced and usually observed in the reaction with organylhalides under drastic conditions ( $>250^\circ\text{C}$ ), often in which I<sub>2</sub> is added to increase the yield of the target products PX<sub>3</sub> and R<sub>4</sub>PX.<sup>9f,54</sup> In 1979, Fluck et al. reported on *ab initio* calculations of the protonation of P<sub>4</sub>.<sup>55</sup> They concluded that a preferred protonation proceeds at an apex of the P<sub>4</sub> molecule, followed by an edge protonation, whereas an attack of H<sup>+</sup> at a P<sub>3</sub> face was excluded. In 1996, Abboud et al. calculated the gas-



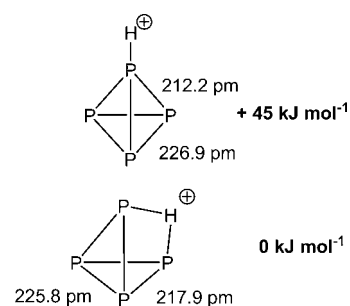
**Figure 3.** Grading of the stability of even-numbered  $P_n$  moieties with  $n \geq 8$  in comparison to tetrahedral  $P_4$ . Energies are given in  $\text{kJ mol}^{-1}$  ( $P_4$ ) relative to  $P_4$  calculated at the SCF/SVP level of theory.

**Scheme 1. General Reactivity Pattern of  $P_4$  Phosphorus Revealing Electrophilic and Nucleophilic Reactivity as Well as Radical Bond Breaking**



phase basicity of  $P_4$  by using MP2/6-31G(d,p) methods and showed that a  $H^+$  bridged opened P–P edge structure is, by  $45.2 \text{ kJ mol}^{-1}$ , more stable than an apex-attached molecule (Figure 4).<sup>56</sup>

Often the reaction of  $P_4$  with the electrophilic reagents is accompanied by the presence of nucleophiles such as  $HO^-$ . The combined action of electrophiles and nucleophiles leads to a consecutive splitting of all P–P bonds to obtain  $P_1$  moieties. Since the experimental details of these few reactions with electrophiles as well as the electrochemical activation of  $P_4$  are well summarized in a review on organophosphorus compounds,<sup>9f</sup> the present review will focus on more recent results in this area. In contrast, according to experimental findings, the major reactivity pattern of tetrahedral  $P_4$  is its electrophilicity. Thus, nucleophiles attack predominantly an apex P atom or an edge of the  $P_4$  tetrahedron (Scheme 1). Moreover, full breaking of a P–P single bond, initialized, for example, by UV



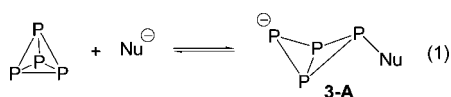
**Figure 4.** Energetic differences (MP2/6-31G(d,p) level of theory) of protonated  $P_4$  structures; adapted from ref 56.

radiation, is a high energy process<sup>57</sup> and would lead to a biradical, which can be alternatively represented as zwitterionic structures (Scheme 1).

In light of unknown and undetermined mechanistic aspects of the  $P_4$  reactivity in most of the published experimental details in the present review, it is difficult to classify it into electrophilic, nucleophilic, and redox activation, respectively. In the following, this problem will be avoided by an arrangement of the reactions according to the main group number of the substrate reacting with  $P_4$ . However, because recent results show degradation of  $P_4$  by special nucleophiles in the following, these data will be discussed according to the aspect of the maintenance of  $P_4$  or polyphosphorus structural units. Therefore, for the latter, conclusions on possible mechanisms can be drawn.

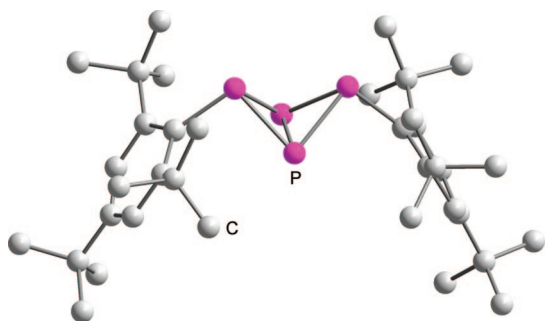
### 3.2. Degradation of P<sub>4</sub> Phosphorus by Nucleophiles under Maintenance of P<sub>n</sub> Structural Moieties

Although the phosphorus atoms in the P<sub>4</sub> tetrahedron exhibit a lone pair of electrons, P<sub>4</sub> mainly shows an electrophilic character and can be attacked by nucleophiles. If the nucleophile is charged, the nucleophilic attack occurs at one of the phosphorus atoms and causes the opening of the tetrahedron, leading to a butterfly like bicyclo[1.1.0]tetraphosphabutane moiety **3-A** (eq 1). Although the subsequent reactivity is reduced, **3-A** is still reactive against nucleophiles and different reaction pathways are opened which lead to different products depending on the nature of the nucleophiles, trapping reagents, and reaction conditions used. Strong nucleophiles shift the equilibria (eq 1) to the right whereas weak nucleophiles shift the reaction to the left. In the latter case, the presence of electrophiles is required in order to degrade P<sub>4</sub>.



The degradation of P<sub>4</sub> can hardly be stopped at the stage of **3-A**. Nevertheless, if the bulky organic nucleophile 2,4,6-*t*Bu<sub>3</sub>C<sub>6</sub>H<sub>2</sub>Li is reacted with P<sub>4</sub> in the presence of the corresponding aryl bromide as an electrophile, it is possible to stop the degradation of P<sub>4</sub> by the stage **3-A**.<sup>58</sup> The structure of the resulting bicyclo[1.1.0]tetraphosphabutane is depicted in Figure 5. A structure of type **3-A** is also proposed for the pentaphosphide, KP<sub>5</sub>H<sub>2</sub>, prepared from KPH<sub>2</sub> and P<sub>4</sub> in DMF.<sup>59</sup> Even though it was only characterized by <sup>31</sup>P NMR spectroscopy and molecular weight determinations, the tetraphosphanide HP<sub>4</sub><sup>-</sup> featuring a structure of type **3-A** is also known; however, it was not synthesized by the direct reaction of P<sub>4</sub> with H<sup>-</sup> but by reduction of P<sub>4</sub> with Na/K naphthalenide.<sup>60</sup>

Reacting P<sub>4</sub> with strong nucleophiles such as sodium hydroxide or sodium ethoxide in EtOH generates a dark red solution which is suggested to contain uncharacterized metastable phosphanides, which decompose slowly to H<sub>2</sub>, PH<sub>3</sub>, and Na<sub>3</sub>PO<sub>2</sub>.<sup>61</sup> The addition of electrophiles such as MeI to these red solutions followed by oxidation with HNO<sub>3</sub> gives a mixture of MePH<sub>2</sub>, MePO<sub>3</sub>H<sub>2</sub>, Me<sub>2</sub>PO<sub>2</sub>H, and Me<sub>3</sub>PO. The electron deficient alkylating agents acrylonitrile, acrylamide, ethyl acrylate, and vinylphosphonate are also used as trapping reagents, giving mainly the corresponding phosphine oxides as the reaction product.<sup>62</sup> Similarly, allyl halides and 2-chloro-5-(chloromethyl)thiophene react with

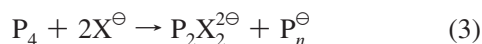
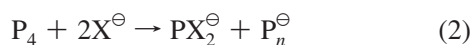


**Figure 5.** Molecular structure of (2,4,6-*t*Bu<sub>3</sub>C<sub>6</sub>H<sub>2</sub>)<sub>2</sub>P<sub>4</sub> as type **3-A** compound; adapted from ref 58. Hydrogen atoms are omitted for clarity.

white phosphorus in the presence of hydroxide (superbase media) mainly to give a mixture of tris(propen-2-yl), bis(propen-2-yl)(*E*-propen-1-yl), and bis(*E*-propen-1-yl)(propen-2-yl)phosphine oxides and tris[(5-chloro-2-thienyl)methyl]phosphine oxide, respectively.<sup>63</sup> Furthermore, non-typical weak electrophiles such as styrene, vinylpyridines, and phenylacetylene were used to functionalize P<sub>4</sub> in superbase media.<sup>64</sup> Tertiary phosphine oxides are the main reaction products of the reaction of *N*-hydroxymethyldialkylamines with P<sub>4</sub> along with phosphonic and phosphinic acids.<sup>65</sup> Weaker nucleophiles such as methanol or ethanol react with white phosphorus only by heating, giving a mixture of the corresponding alkylphosphines and phosphonium salts.<sup>66</sup> The reaction of amines with P<sub>4</sub> leads to insoluble precipitates which are proposed to be another modification of phosphorus.<sup>67</sup> A reaction mechanism with the formation of an intermediate of type **3-A** is proposed. However, if the reaction of P<sub>4</sub> with NH<sub>3</sub> is performed at pressures higher than 5 kbar and temperatures above 250 °C, the hexaaminocyclotriphosphazene P<sub>3</sub>N<sub>3</sub>(NH<sub>2</sub>)<sub>6</sub>·0.5NH<sub>3</sub> is formed among red phosphorus.<sup>68</sup>

The degradation of P<sub>4</sub> phosphorus is also proceeded by carbon centered nucleophiles such as organolithium or organomagnesium compounds to give dark red solutions believed to be complex organophosphanides.<sup>69</sup> Quenching these solutions with alkylating agents leads to mixed tertiary phosphines, while hydrolysis gives primary phosphines with small amounts of secondary and tertiary phosphines. Depending on the reaction conditions, cyclotetraphosphanes (RP)<sub>4</sub> (R = Et, Pr, Bu) are also formed.<sup>70</sup> In each case, the main side product of this reaction is an insoluble amorphous yellow solid. The examined reaction of P<sub>4</sub> with MeLi and *t*BuLi shows that oligophosphides and partly alkylated oligophosphides mainly containing the nortricyclane P<sub>7</sub> unit are formed. This is then trapped with Me<sub>3</sub>SiCl to give the corresponding phosphines.<sup>71</sup> The reaction of P<sub>4</sub> with alkali metal acetylides followed by treatment with alkyl halide leads to the formation of acetylenic phosphines (RC≡C)PR'<sub>2</sub> and (RC≡C)<sub>2</sub>PR' (R = R' = Et; R = Et, R' = Pr; R = Ph, R' = Et). The phosphides (RC≡C)P<sup>2-</sup> and (RC≡C)<sub>2</sub>P<sup>-</sup> were proposed to be intermediates in these reactions.<sup>72</sup> Reacting lithium (trimethylsilyl)diazomethanide Li[Me<sub>3</sub>SiCN<sub>2</sub>] with P<sub>4</sub> leads to the formation of the 1,2,3,4-diazadiphospholide anion, which can easily be protonated by trifluoroacetic acid to 2H-1,2,3,4-diazadiphosphole.<sup>73</sup> The degradation of P<sub>4</sub> by cyanides proceeds much cleaner, leading to the dicyanophosphanide P(CN)<sub>2</sub><sup>-</sup> and the polyphosphide P<sub>15</sub><sup>-</sup> (eq 2; X = CN).<sup>74</sup> Similar to cyanides, Ph<sub>2</sub>P<sup>-</sup> reacts with P<sub>4</sub> to form the triphosphide (Ph<sub>2</sub>P)<sub>2</sub>P<sup>-</sup>, the diphosphane (Ph<sub>2</sub>P)<sub>2</sub>, and polyphosphides (eq 2; X = Ph<sub>2</sub>P). Linear phosphides of the type (PhP)<sub>n</sub><sup>2-</sup> (n = 1, 2, and 3) react with P<sub>4</sub> by extending their chain length up to n = 4, whereas (PhP)<sub>4</sub><sup>2-</sup> reacts with P<sub>4</sub> to form the cyclopentaphosphide Ph<sub>4</sub>P<sub>5</sub><sup>-</sup>.<sup>75</sup> If phosphorus undergoes disproportionation reactions, this behavior toward nucleophiles can be rationalized in the following way: the oxidized 4-electron P<sup>+</sup> species is stabilized by the addition of two ligand molecules X<sup>-</sup> to give the closed shell moiety PX<sub>2</sub><sup>-</sup> and the reduced P<sup>3-</sup> species tries to distribute the high charge by its transfer to other P atoms. As a result, polyphosphides are formed. This proceeds if an excess of the nucleophile is used (eq 2). Using R<sub>2</sub>POM (M = Li, Na; R = Et, Ph) as nucleophiles, the degradation of P<sub>4</sub> can be stopped at the stage of a P<sub>2</sub> unit, and P<sub>2</sub>X<sub>2</sub><sup>2-</sup> species are formed if a deficit of the nucleophile is used (eq 3; X =

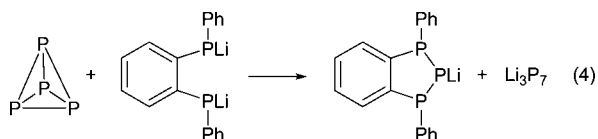
$R_2PO$ ).<sup>76</sup> Thus, as a result,  $M_2[OP(R_2)PP(R_2)PO]$  and  $M[OP(R_2)P(R_2)PO]$  are formed together with polyphosphanides such as  $P_7^{3-}$  and  $P_{16}^{2-}$ , respectively. The products are characterized by  $^{31}P$  NMR spectroscopy.



It could be shown that small carbon anions  $C_n^-$  ( $n = 3-9$ ) react with gaseous  $P_4$  under the conditions of Fourier transform ICR mass spectrometry to give carbon phosphide anions such as  $C_nP^-$ ,  $C_nP_2^-$ ,  $C_nP_5^-$  ( $n = 3-9$ ), and  $C_4P_4^-$ .<sup>77</sup> The stability and structure of these anions have been investigated by theoretical methods.

The reaction of weak nucleophiles with  $P_4$  is strongly accelerated by the presence of electrophiles in the reaction media. The common electrophile that is widely used is  $CCl_4$ .<sup>9c,e</sup> The reaction mechanism is not clear, but a series of nucleophilic attacks with P-P bond cleavages and combinations of the formed phosphides with the electrophilic reagent, followed by nucleophilic substitutions is proposed. Usually this type of reaction leads to the complete degradation of  $P_4$  to compounds containing one phosphorus atom. Reacting  $P_4$  with amines in the presence of  $CCl_4$  followed by hydrolysis leads to trisamides of phosphoric acid. The additional use of the HF donator  $Et_3NH^+F^-$  leads to the formation of  $HPF_5^-$ ,  $R_2NH^+PF_5^-$ , and  $(R_2NH)_2P(O)F$ .<sup>78</sup>  $P_4$  reacts similarly with  $NaOR$ <sup>79</sup> or  $NaSR$ <sup>80</sup> in the presence of  $CCl_4$  to give  $(RO)_3P$  and  $(RS)_3P$ , respectively.  $(RO)_3P$  can be converted to  $(RO)_2(O)PH$  by hydrolysis, whereas  $(RS)_3P$  gives  $(RS)_3PO$  under oxidizing conditions.

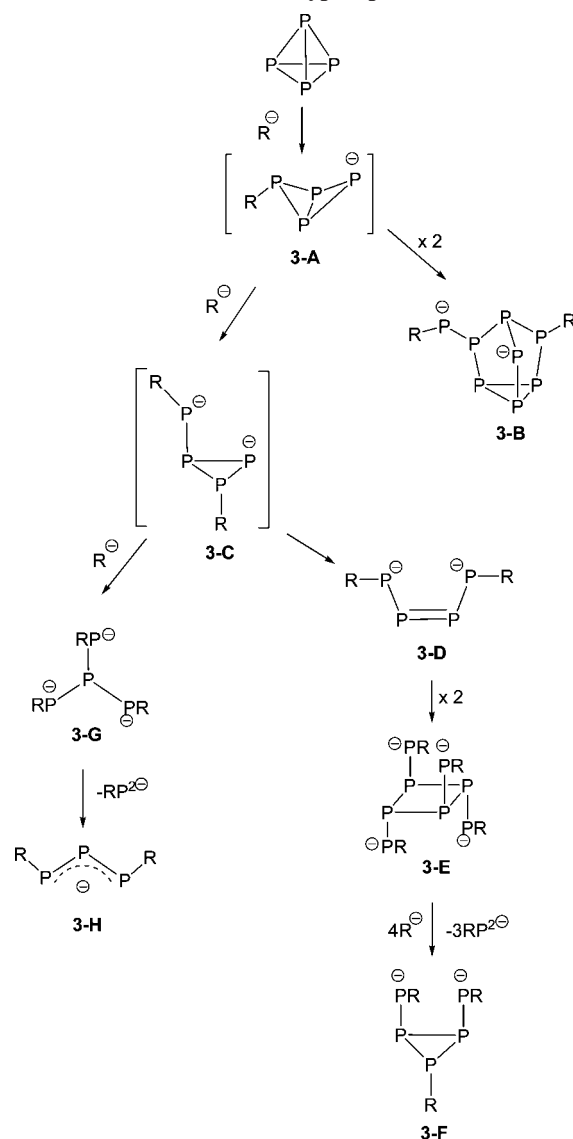
Phosphorus centered nucleophiles such as phosphanides are able to react with  $P_4$ , leading to P-P bond formation and, as consequence, to phosphorus-rich compounds. Thus *o*-phenylene-bis(lithiumphenylphosphanide) reacts with  $P_4$  under formation of a benzotriphosphole derivative shown in eq 4. In addition,  $Li_3P_7$  is formed.<sup>81,76b</sup> Larger oligophosphides can be obtained by the reaction of  $Cs_4P_6$  or  $Na_3P_7$  with  $P_4$  in en to give the phosphorus rich phosphides  $Cs_3P_{11}(en)_3$  and  $M_4P_{14}(en)_x$  ( $M = Na, Cs$ ), respectively.<sup>82</sup> Alkali metal phosphides are also used as a phosphorus source by the reaction of  $P_4$  with alkali metals.



A more controllable degradation of  $P_4$  phosphorus is achieved by reacting the bulky, silicon centered nucleophiles  $tBu_3Si^-$ ,  $tBu_2PhSi^-$ , or  $(Me_3Si)_3Si^-$  with  $P_4$ . The nature of the reaction products and the degree of the degradation of the  $P_4$  tetrahedron is strongly dependent on the stoichiometry and the solvent used. High amounts of silanide  $R_3Si^-$  and polar solvents favor stronger degradation whereas a deficit of silanide and less polar solvents degrade  $P_4$  to a lesser extent. Here, the use of bulky silanides allows a deeper insight into the mechanism and pathways of the nucleophilic degradation of  $P_4$ , and comprehensive conclusions can be drawn from the individual results, which are summarized in Scheme 2.

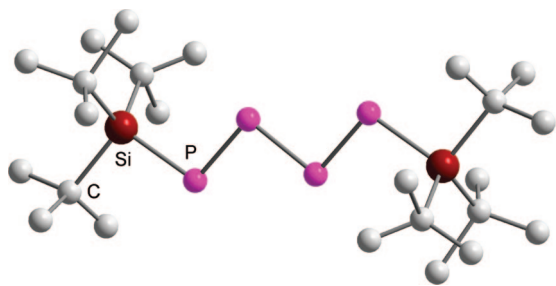
Although compounds of type **3-A** are not isolated by the reaction of silanides with  $P_4$ , it is postulated to be an

**Scheme 2. Schematic Degradation of  $P_4$  by Silanides ( $R = R_3Si$ ) under Maintenance of Polyphosphorus Units**

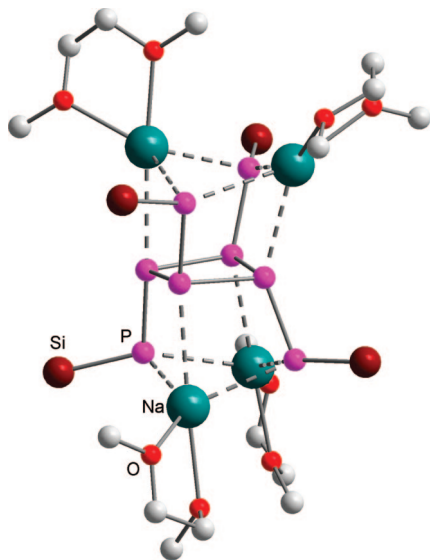


intermediate by the reaction of  $P_4$  with  $[(Me_3Si)_3SiK(18-crown-6)]$ , leading to the octaphosphide **3-B** ( $R = (Me_3Si)_3Si$ ). Compound **3-B** is proposed to be the dimerization product of **3-A**, followed by rearrangements through intramolecular nucleophilic attacks.<sup>83</sup> The addition of 2 equiv of  $tBu_3SiM$  ( $M = Na, K$ ) to  $P_4$  results in the formation of **3-C** as an intermediate. Although a stable compound of type **3-C** could not be isolated, the core structure can be found in different organophosphanes of the type  $P_3R_2(PR_2)$ .<sup>84</sup> Reorganization of **3-C** leads to the formation of the tetraphosphenediide **3-D**, which is known for  $R = tBu_3Si$ ,  $tBu_2PhSi$ ;  $M = Li, Na, K, Rb, Cs$ , and  $Ba$ .<sup>85</sup> According to  $^{31}P$  NMR spectroscopic studies,  $Na_2[(tBu_3Si)_2P_4]$  adopts a *cis* configuration in THF solutions, but the ion separated compound  $[Na(18-crown-6)(THF)_2]_2[(tBu_3Si)_2P_4]$  adopts a *trans* configuration in the solid-state. The structure of the **3-D**-type anion in  $[Na(18-crown-6)(THF)_2]_2[(tBu_3Si)_2P_4]$  is depicted in Figure 6.<sup>85d</sup> **3-D** is stable in THF, but it dimerizes in weakly polar solvents to the octaphosphide **3-E**. This reaction is reversible, and in less polar solvents, **3-E** can be converted via a [2 + 2] retrocycloaddition to **3-D**. The straightforwardness of this equilibrium is ascribed to the cluster-like structure of  $M_4(\mathbf{3-E})$ .<sup>85a</sup> The structure of the **3-E**-type compound





**Figure 6.** Molecular structure of the anion in  $[\text{Na}(\text{18-crown-6})(\text{THF})_2]_2[(t\text{Bu}_3\text{Si})_2\text{P}_4]$ ; adapted from ref 85d. Hydrogen atoms are omitted for clarity.



**Figure 7.** Molecular structure of  $[\text{Na}(\text{DME})_4]_4[(t\text{Bu}_3\text{Si})_4\text{P}_8]$ ; adapted from ref 85a. Hydrogen atoms and *t*Bu groups are omitted for clarity.

$[\text{Na}(\text{DME})_4]_4[(t\text{Bu}_3\text{Si})_4\text{P}_8]$  (DME = 1,2-dimethoxyethane) is depicted in Figure 7.

The pentaphosphide  $(t\text{Bu}_3\text{Si})_3\text{P}_5\text{Na}_2$  (type **3-F**) is formed by increasing the  $t\text{Bu}_3\text{SiNa}/\text{P}_4$  molar ratio to 4:1 in benzene.<sup>86</sup> Alternative synthesis of **3-F** is achieved by protolysis of the tetraphosphide  $(t\text{Bu}_3\text{Si})_2\text{P}_4\text{Na}_2(\text{THF})_n$  (type **3-D**) with  $\text{CF}_3\text{CO}_2\text{H}$  in THF or by dissolving crystals of  $(t\text{Bu}_3\text{Si})_2\text{P}_4\text{Na}_2(\text{THF})_n$  in toluene. Degradation of **3-E** with silanide also leads to the formation of **3-F**, which is known for  $\text{R} = t\text{Bu}_3\text{Si}$  and  $\text{M} = \text{Na}, \text{K},$  and  $\text{Ag}$ .<sup>85b,c,87</sup> Both  $(t\text{Bu}_3\text{Si})_3\text{P}_5\text{Na}_2$  and  $(t\text{Bu}_3\text{Si})_3\text{P}_5\text{Ag}_2$  possess a dimeric structure in the solid state, whereas the former is monomeric in THF. Interestingly,  $(t\text{Bu}_3\text{Si})_3\text{P}_5\text{Na}_2$  (type **3-F**) is quantitatively oxidized by tetracyanoethene to bicyclo[2.1.0]pentaphosphane  $(t\text{Bu}_3\text{Si})_3\text{P}_5$ .<sup>85b</sup> Addition of  $t\text{Bu}_3\text{SiNa}$  to the pentaphosphane re-forms  $(t\text{Bu}_3\text{Si})_3\text{P}_5\text{Na}_2$  (type **3-F**) along with  $t\text{Bu}_3\text{SiSi}(t\text{Bu})_3$ .

Reactions of  $\text{P}_4$  with the silanides  $t\text{Bu}_3\text{SiM}$  ( $\text{M} = \text{Li}, \text{Na}$ ) and  $t\text{Bu}_2\text{PhSiNa}$  in a 1:3 stoichiometry lead to the formation of the corresponding phosphides of type **3-G**.<sup>88</sup> THF solutions of **3-G** ( $\text{R} = t\text{Bu}_3\text{Si}; \text{M} = \text{Li}, \text{Na}$ ) decompose slowly at ambient temperature to the corresponding phosphides of type **3-H** and  $t\text{Bu}_3\text{SiPM}_2$ . Interestingly, the  $t\text{Bu}_2\text{PhSi}$  derivatives of **3-G** decompose to pentaphosphides of type **3-F** rather than to triphosphides of type **3-H**.<sup>88</sup> If the reaction of  $t\text{Bu}_3\text{SiK}$  with  $\text{P}_4$  is performed in a 3:1 stoichiometry in THF, the tetraphosphide **3-D** ( $\text{R} = t\text{Bu}_3\text{Si}; \text{M} = \text{K}$ ) and the octaphosphide **3-E** ( $\text{R} = t\text{Bu}_3\text{Si}; \text{M} = \text{K}$ ) are formed first, which are subsequently slowly decomposed by unreacted  $t\text{Bu}_3\text{SiK}$  at

room temperature to the triphosphide **3-H**, pentaphosphide **3-F**, and monophosphanide  $t\text{Bu}_3\text{SiPK}_2$ .<sup>87</sup>

The degradation of  $\text{P}_4$  from nucleophiles can also be initiated by electrolysis. Under electrocatalytic conditions, nucleophiles such as  $\text{RO}^-$  can be generated. In the presence of electrophilic reagents, these nucleophiles react with  $\text{P}_4$  in a joint action leading to the degradation of  $\text{P}_4$ . The reaction products are various organophosphorus compounds such as esters of phosphoric, phosphorus, and phosphonic acids, tertiary phosphines, and other organophosphorus compounds. By this method, the formation of phosphorus esters containing P–O, P–N, and P–S bonds as well as compounds containing P–C bonds are reported.<sup>89</sup>

## 4. Activation and Degradation of P<sub>4</sub> Phosphorus by Main Group Elements and Compounds

Independent of the reaction mechanism, which is usually not or only partly understood, the following results of  $\text{P}_4$  activation by main group compounds are presented according to the group number of the activating main group element in the compound. Whereas for group 1 and 2 elements a reductive activation of  $\text{P}_4$  occurs, the reaction of the corresponding main group compounds is mainly a nucleophilic degradation of  $\text{P}_4$ . Starting from group 13 element compounds, the majority of cases are based on the attack of a carbene-like moiety at the  $\text{P}_4$  tetrahedron. In contrast, in some cases, electrophilic attack occurs at the  $\text{P}_4$  phosphorus, as in the case of corresponding phosphonium cations.

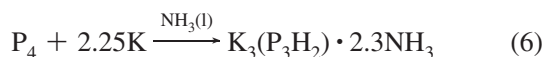
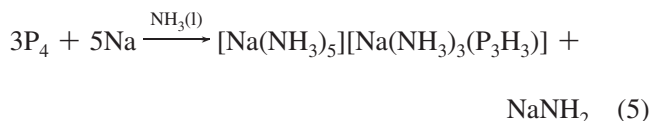
### 4.1. Activation of P<sub>4</sub> Phosphorus by Group 1 and 2 Elements and Compounds

The reaction of alkali metals with white phosphorus leads to alkali metal phosphides or oligophosphides. These reactions can be performed in liquid ammonia as well as in polar organic solvents such as tetrahydrofuran, dimethoxyethane, or ethylenediamine. The nature of the phosphides obtained is strongly dependent on the atomic ratio of phosphorus and alkali metal, the solvent used, the size of the cation, and the reaction conditions. Depending on the reaction conditions, simple phosphides, polycyclic phosphides, and aromatic or pseudoaromatic cyclophosphanes could be obtained. Phosphides of the type  $\text{P}^{3-}$  are produced, usually using a high M/P atomic ratio in the reaction of  $\text{P}_4$  with alkali metals in organic solvents. Reducing the M/P ratio leads to the formation of polyphosphides.

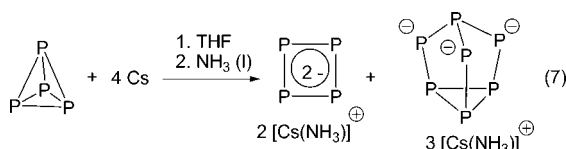
Early results of the reaction of alkali metals (Li, Na, K) in liquid ammonia with toluene solutions of  $\text{P}_4$  describe the formation of phosphides with unknown structures.<sup>90</sup> More recent investigations by using only liquid ammonia as solvent and the atomic ratio of P/Na of 3:5 report on the isolation of  $[\text{Na}(\text{NH}_3)_5][\text{Na}(\text{NH}_3)_3(\text{P}_3\text{H}_3)]$ , containing the *all-trans catena*-triphosphide  $\text{P}_3\text{H}_3^{2-}$  (eq 5).<sup>91</sup> Under similar reaction conditions ( $\text{P}_4/\text{K}$  atomic ratio of 1:2.25), the potassium salt of the *catena*-dihydrogen triphosphide  $\text{P}_3\text{H}_2^{3-}$  is isolated as  $\text{K}_3(\text{P}_3\text{H}_2) \cdot 2.3\text{NH}_3$  and characterized by single crystal X-ray diffraction (eq 6).<sup>92</sup> The Rb and Cs salts of  $\text{P}_3\text{H}_2^{2-}$  [ $\text{Rb}(\text{18-crown-6})_2(\text{P}_3\text{H}_2) \cdot 7.5\text{NH}_3$  and  $[\text{Cs}(\text{18-crown-6})_2(\text{P}_3\text{H}_2) \cdot 7\text{NH}_3]$  as well as the Rb salt of  $\text{P}_3\text{H}_2^{3-}$  are also reported; however, they are synthesized by dissolving diphosphane,  $\text{P}_2\text{H}_4$ , and a cyclohexaphosphide,  $\text{P}_6^{4-}$ , respectively, in liquid ammonia followed by crystallization.<sup>92</sup> Reacting  $\text{P}_4$  with Na in liquid  $\text{NH}_3$  in a 2:1 or 1.5:1 atomic ratio yields the 1,3-diaminotriphosphane  $\text{P}_3\text{H}_3(\text{NH}_2)_2$ ; however, it is only stable



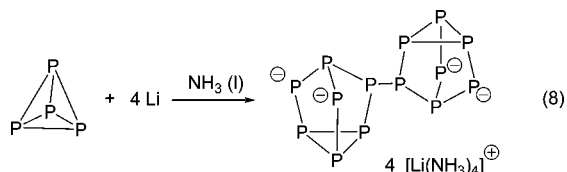
in liquid  $\text{NH}_3$ .<sup>93</sup> According to  $^{31}\text{P}$  NMR spectroscopic investigations from the three possible diastereomers, only the *erythro,erythro* isomer with transoid oriented  $\text{NH}_2$  groups is formed. Side products of this reaction are  $\text{NaPH}_2$ ,  $\text{Na}_2\text{HP}_7$ , and higher phosphides.<sup>94</sup>



The 6- $\pi$  aromatic  $\text{P}_4^{2-}$  in  $\text{Cs}_2\text{P}_4 \cdot 2\text{NH}_3$  is prepared as a side product by reacting  $\text{P}_4$  with cesium in THF followed by solvation in liquid ammonia (eq 7). The main product of this reaction is  $\text{Cs}_3\text{P}_7 \cdot 3\text{NH}_3$ . An alternative synthesis of  $\text{Cs}_2\text{P}_4 \cdot 2\text{NH}_3$  is the reaction of the diphosphane  $\text{P}_2\text{H}_4$  with metallic cesium.<sup>95</sup>



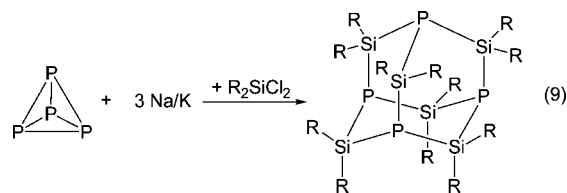
The phosphorus rich phosphide  $\text{P}_{14}^{4-}$  is obtained by reacting Li with  $\text{P}_4$  in a 1:1 atomic ratio in liquid ammonia (eq 8). The  $\text{P}_{14}^{4-}$  anion in  $[\text{Li}(\text{NH}_3)_4]_4\text{P}_{14} \cdot \text{NH}_3$  consists of two nortricyclane-like ( $\text{P}_7^{3-}$ ) units which are bound by a P–P bond.<sup>96</sup> At room temperature,  $[\text{Li}(\text{NH}_3)_4]_4\text{P}_{14} \cdot \text{NH}_3$  eliminates ammonia, but by dissolving the obtained solid in liquid ammonia, the starting material is re-formed in quantitative yield. The sodium salt of  $\text{P}_{14}^{4-}$ , i.e.  $\text{Na}_4(\text{DME})_8\text{P}_{14}$ , is synthesized by reacting sodium naphthalene with white phosphorus in 1,2-dimethoxyethane (DME).<sup>97</sup>



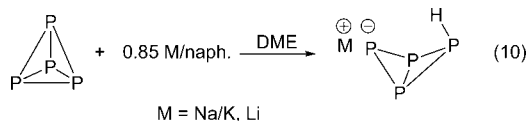
The product distribution of the reaction of  $\text{P}_4$  with alkali metals is also influenced by the solvent and reaction temperature used. Solvents with low boiling points, such as ammonia, lead to relatively small phosphides, whereas solvents with higher boiling points usually produce higher aggregated polyphosphides, depending on the P/M ratio.

Reacting white phosphorus with Na in a 1:3 ratio in inert organic solvents such as benzene, THF, or 1,2-dimethoxyethane, the phosphide  $\text{Na}_3\text{P}$  is obtained, which is subsequently quenched by alkyl halides to give a varying mixture of tetramethyl- and trimethylphosphonium salts.<sup>98</sup> The reaction of a Na/K alloy with white phosphorus (P/M = 1:3) in boiling THF or DME leads to the formation of the phosphides  $\text{M}_3\text{P}$ , which can subsequently be reacted with  $\text{Me}_3\text{SiCl}$  to give  $(\text{Me}_3\text{Si})_3\text{P}$ .<sup>99</sup> If a 1:0.6 atomic ratio of P to M is used and the reaction mixture is reacted with  $\text{Me}_3\text{SiCl}$  among  $(\text{Me}_3\text{Si})_3\text{P}$  and  $(\text{Me}_3\text{Si})_2\text{P}-\text{P}(\text{SiMe}_3)_2$ , the higher phosphanes  $(\text{Me}_3\text{Si})_3\text{P}_7$ ,  $(\text{Me}_3\text{Si})_4\text{P}_{14}$ , and  $(\text{Me}_3\text{Si})_5\text{P}_{13}$  can be isolated.<sup>100</sup> Using  $(\text{Me}_3\text{Si})_3\text{SiCl}$  instead of  $\text{Me}_3\text{SiCl}$  as quenching reagent, the nortricyclane derivative  $\{(\text{Me}_3\text{Si})_3\text{Si}\}_3\text{P}_7$  is isolated and

structurally characterized.<sup>101</sup> Similarly, quenching the in situ generated mixture of phosphides generated from  $\text{P}_4$  and Na/K alloys with  $\text{RR}'\text{SiCl}_2$  leads to the polycyclic silylphosphanes  $(\text{Me}_2\text{Si})_3\text{P}_4$ ,  $(\text{RR}'\text{Si})_6\text{P}_4$  ( $\text{R} = \text{Me}$ ,  $\text{R}' = \text{Et}$ ;  $\text{R} = \text{R}' = \text{Et}$ ,  $\text{R} = \text{Ph}$ ,  $\text{R}' = \text{Me}$ ;  $\text{R} = \text{vinyl}$ ,  $\text{R}' = \text{Me}$ ;  $\text{R} = \text{Me}$ ,  $\text{R}' = \text{H}$ ),<sup>103</sup> and  $(\text{MeHSi})(\text{Et}_2\text{Si})_5\text{P}_4$ , with the latter two revealing an adamantane-like structure (eq 9). The triphosphanortricyclane  $\text{CH}_3\text{C}(\text{CH}_2\text{P})_3$  is also reported by the in situ reaction of  $\text{P}_4$  with Na/K alloy followed by a reaction with  $\text{CH}_3\text{C}(\text{CH}_2\text{Br})_3$ . However, the yield is low.<sup>104</sup>

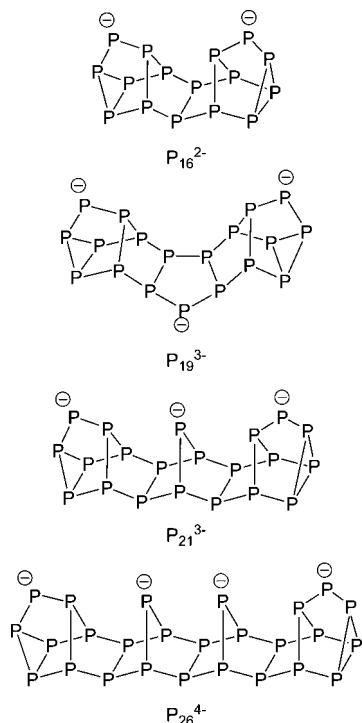


The first step of the reaction of  $\text{P}_4$  phosphorus with alkali metals is expected to be a one- or two-electron transfer, leading to the formation of a radical anion or dianion, respectively, with a butterfly-like structure. This radical anion or dianion could not be isolated; however, the tetraphosphide  $\text{MHP}_4$  ( $\text{M} = \text{Na/K, Li}$ ) is synthesized by reacting  $\text{P}_4$  with a solution of sodium/potassium naphthalenide or lithium naphthalenide in DME (eq 10).<sup>60</sup>  $\text{HP}_4^-$  represents formally the first reaction product of white phosphorus with the nucleophile  $\text{H}^-$ .  $\text{MHP}_4$  is stable only at low temperatures and decomposes to phosphorus rich phosphides, mainly to  $\text{M}_2\text{P}_{16}$  and  $\text{MP}_5$ .



The phosphorus rich phosphide  $\text{Na}_2\text{P}_{16} \cdot 8\text{THF}$  can be isolated by the reaction of  $\text{P}_4$  with sodium (3:1 atomic ratio) in THF in the presence of 18-crown-6. The structure of the  $\text{P}_{16}^{2-}$  anion is built up from two deltacyclane units which contain a joint  $\text{P}_2$  bridge (Figure 8), as it is determined by  $^{31}\text{P}$  NMR spectroscopy.<sup>105</sup> The structure of the analogous  $(\text{Ph}_4\text{P})_2\text{P}_{16}$  is determined by single crystal X-ray diffractions.<sup>106</sup> The lithium salt of the  $\text{P}_{16}^{2-}$  anion can also be synthesized from  $\text{P}_4$  and  $\text{LiPH}_2$  (23:12 molar ratio)<sup>107</sup> or by cleavage of  $\text{P}_4$  with  $\text{LiP}(\text{SiMe}_3)_2$ .<sup>108</sup> The latter synthetic method strongly depends on the concentration of the starting materials and their molar ratio. Using a  $\text{P}_4/\text{LiP}(\text{SiMe}_3)_2$  1:0.5 ratio of the reactants,  $\text{Li}_2\text{P}_{16} \cdot 7\text{THF}$  can be obtained, which by further addition of  $\text{LiP}(\text{SiMe}_3)_2$  leads to rearrangements and decomposition and finally to  $\text{Li}_3\text{P}_7$ ,  $\text{Li}_2\text{P}_7(\text{SiMe}_3)$ , and  $\text{P}(\text{SiMe}_3)_3$ . Using an excess of  $\text{LiPH}_2$  in the reaction with  $\text{P}_4$  leads to the formation of  $\text{Li}_3\text{P}_7$  in high yield.<sup>109</sup>

A mixture of higher aggregated polyphosphides containing  $\text{M}_3\text{P}_{19}$ ,  $\text{M}_2\text{P}_{16}$ ,  $\text{M}_3\text{P}_{21}$ ,  $\text{M}_4\text{P}_{26}$ ,  $\text{M}_2\text{HP}_7$ ,  $\text{MH}_2\text{P}_7$ , and  $\text{M}_2\text{H}_2\text{P}_{14}$  ( $\text{M} = \text{Li, Na, K}$ ), among other unidentified polyphosphides, is synthesized by reacting Na, K, or  $\text{LiPH}_2$  with  $\text{P}_4$  (in a molar ratio varying from 2.5:1 to 1:2) in THF or DME.<sup>110</sup> The isolation of the individual phosphides is not achieved, but the mixture can be enriched for  $\text{M}_2\text{P}_{16}$ ,  $\text{M}_3\text{P}_{21}$ , and  $\text{M}_3\text{P}_{19}$ . Using a P/Na ratio of 2:1 leads to a mixture of polyphosphides from which  $\text{Na}_3\text{P}_{21} \cdot 15\text{THF}$ <sup>111,112</sup> (Figure 8) and a solution containing the aromatic  $\text{P}_5^-$  anion<sup>113,39a</sup> can be isolated.  $\text{NaP}_5$  as a pure 18-crown-6 complex is prepared by reacting white phosphorus with  $\text{NaPH}_2$  ( $\text{P}/\text{NaPH}_2 = 5:1$  to 5.6:1) in boiling THF in the presence of 18-crown-6.<sup>39c,d</sup>



**Figure 8.** Structures of the polyphosphides  $P_{16}^{2-}$ ,  $P_{19}^{3-}$ ,  $P_{21}^{3-}$ , and  $P_{26}^{4-}$ .

Interestingly, the reaction of Na with an excess of P<sub>4</sub> in diglyme leads, among the above-mentioned polyphosphides and P<sub>5</sub><sup>-</sup>, to the 1,2,3,4-tetraphospha-(P<sub>4</sub>CH<sup>-</sup>) and 1,2,3-triphosphacyclopentadienide (P<sub>3</sub>(CH)<sub>2</sub><sup>-</sup>) anions.<sup>113,114</sup> Li<sub>3</sub>P<sub>19</sub> can also be synthesized by reacting Li<sub>3</sub>P<sub>7</sub> with P<sub>4</sub>, I<sub>2</sub>, or 1,2-dibromoethane and by the reaction of Li<sub>2</sub>P<sub>16</sub> with LiPH<sub>2</sub>. Li<sub>3</sub>P<sub>21</sub> is also accessible from Li<sub>3</sub>P<sub>7</sub> and I<sub>2</sub> or 1,2-dibromoethane and by metalation of P<sub>7</sub>H<sub>3</sub> with LiPH<sub>2</sub> or BuLi. Partial alkylation of Na<sub>3</sub>P<sub>21</sub> with alkyl halides is also possible.<sup>115</sup> Using a molar ratio of P<sub>4</sub>/LiPH<sub>2</sub> or P<sub>4</sub>/Na varying from 1.4:1 to 1:1.5, the polyphosphides Li<sub>4</sub>P<sub>26</sub> and Na<sub>4</sub>P<sub>26</sub> are synthesized and the lithium salt is isolated as Li<sub>4</sub>P<sub>26</sub>·16THF (Figure 8).<sup>116</sup> A more convenient route to synthesize and isolate Li<sub>4</sub>P<sub>26</sub>·16THF is the decomposition of LiH<sub>2</sub>P<sub>7</sub> in THF. Unexpectedly, the reaction of P<sub>4</sub> with K in THF/DME followed by extraction with wet EtOH leads to K<sub>2</sub>P<sub>16</sub>. Exchanging the solvent EtOH against THF leads to the clean conversion of K<sub>2</sub>P<sub>16</sub> to K<sub>3</sub>P<sub>21</sub> and elemental phosphorus.<sup>117</sup>

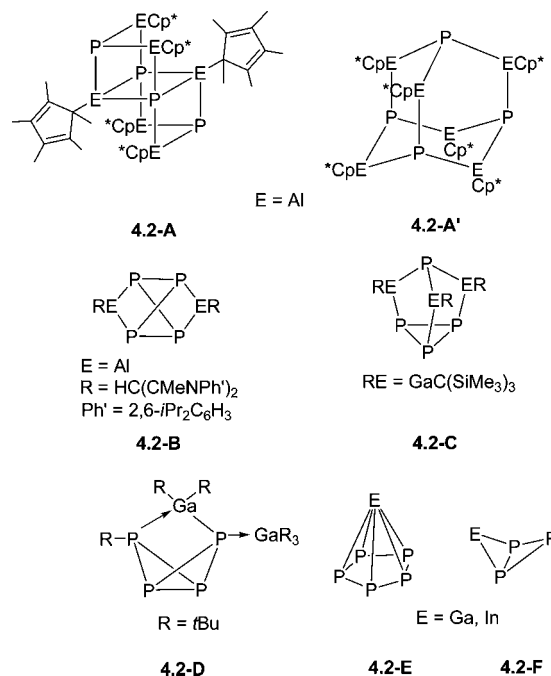
The activation of white phosphorus by group 2 elements is not as widespread as that by the alkali metals. In fact, no reaction is reported in which P<sub>4</sub> is reacted exclusively with a group 2 metal. However, white phosphorus is used as a phosphorus source by dehalogenation of alkyl dihalophosphanes with magnesium in order to obtain phosphorus rich polycyclic phosphanes. The dehalogenation of *t*BuPCL<sub>2</sub> with Mg in the presence of P<sub>4</sub> leads to a mixture of organophosphanes<sup>42,118</sup> from which P<sub>9</sub>*t*Bu<sub>7</sub>, P<sub>10</sub>*t*Bu<sub>8</sub>,<sup>119</sup> and P<sub>13</sub>*t*Bu<sub>9</sub><sup>120</sup> are isolated and spectroscopically characterized. The nature and distribution of the products depends considerably on the bulkiness of the organic group and on the reaction conditions. Thus, the reduction of *i*PrPCL<sub>2</sub> with Mg in the presence of P<sub>4</sub> followed by thermolysis of the reaction mixture leads, depending on the reaction conditions, to the polycyclic phosphanes P<sub>11</sub>*i*Pr<sub>3</sub>,<sup>121</sup> P<sub>11</sub>*i*Pr<sub>5</sub>,<sup>122</sup> P<sub>12</sub>*i*Pr<sub>4</sub>,<sup>123,124</sup> P<sub>13</sub>*i*Pr<sub>5</sub>,<sup>123</sup> P<sub>14</sub>*i*Pr<sub>4</sub>,<sup>125</sup> P<sub>14</sub>*i*Pr<sub>6</sub>,<sup>126</sup> P<sub>18</sub>*i*Pr<sub>6</sub>,<sup>127</sup> and P<sub>20</sub>*i*Pr<sub>6</sub>.<sup>128</sup> Similarly, the reduction of RPCL<sub>2</sub> (R = Me, Et) with Mg in the presence of P<sub>4</sub> leads, among monocyclic phosphanes,<sup>42</sup> to P<sub>9</sub>R<sub>5</sub>, P<sub>10</sub>R<sub>6</sub>,

P<sub>10</sub>R<sub>4</sub>, P<sub>11</sub>R<sub>5</sub>, P<sub>12</sub>R<sub>4</sub>, and P<sub>13</sub>R<sub>5</sub> (R = Me, Et, CHMe<sub>2</sub>).<sup>129</sup> The thermolysis of the cyclopentaphosphane (EtP)<sub>5</sub> with P<sub>4</sub> leads to P<sub>7</sub>Et<sub>3</sub> along with P<sub>9</sub>Et<sub>3</sub>.<sup>130</sup> In this reaction, P<sub>9</sub>Et<sub>3</sub> is obtained as a mixture of two configurational isomers, which undergo inversion on heating.

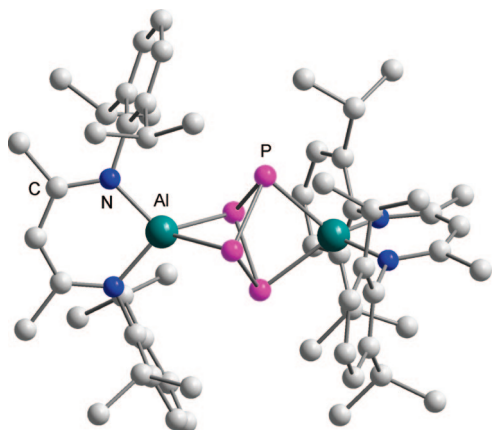
## 4.2. Activation of P<sub>4</sub> Phosphorus by Group 13 Element Compounds

Monovalent group 13 element compounds with relatively small substituents such as organyl groups or Cp\* are electron deficient and aggregate in the solid-state to tetrahedral (E = Al, Ga) or octahedral (E = Ga) clusters. If they possess bulky substituents, such as terphenyls, dimers or monomers are formed. In solution, they deoligomerize to give monomer–oligomer equilibria. These species are able to multiply insert into the P–P bonds of the P<sub>4</sub> tetrahedron. Thus, Schnöckel et al. found that (Cp\*Al)<sub>4</sub> cleaves all P–P bonds in P<sub>4</sub> to yield the electron deficient cage compound (Cp\*Al)<sub>6</sub>P<sub>4</sub> **4.2-A**, which structure consists of two face-sharing heterocubanes with two opposite corners unoccupied (Figure 9).<sup>131</sup> Two of the Al atoms possess η<sup>1</sup> coordinated Cp\* in a 3-fold substitution pattern, whereas the others are η<sup>5</sup> bound. The unusual structure of the insoluble compound **4.2-A** is comparable to that of the adamantane-like isomer **4.2-A'** calculated by DFT, which was chemically more expected. However, by 30–80 kJ mol<sup>-1</sup>, it is higher in energy than **4.2-A**. By using the sterically more bulky nacnac Al(I) species [HC(CMeNPh')<sub>2</sub>Al] (Ph' = 2,6-*i*Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>), an insertion of the RAl unit in two opposite P–P bonds of the P<sub>4</sub> tetrahedron is reported by Roesky et al.<sup>132</sup> The formed insoluble product **4.2-B** (Figure 10) represents an oxidative addition derivative containing RAl(III) species and a P<sub>4</sub><sup>4-</sup> moiety, which is confirmed by <sup>27</sup>Al MAS NMR measurements. The calculated binding energy (127.3 kJ mol<sup>-1</sup>) shows the strong interaction between P<sub>4</sub> and the Al atoms.

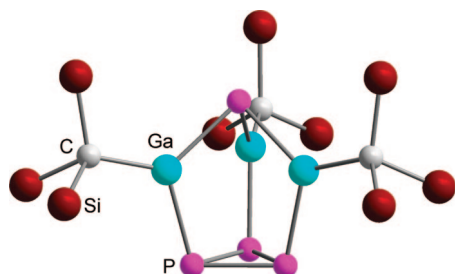
The tetragallane Ga<sub>4</sub>[C(SiMe<sub>3</sub>)<sub>3</sub>]<sub>4</sub> reacts with P<sub>4</sub> phosphorus by a 3-fold insertion of the monovalent Ga unit into P–P



**Figure 9.** X-ray crystallographically verified structures of group 13 element polyphosphorus compounds **4.2-A–D**. Species **4.2-A'**, **4.2-E**, and **4.2-F** are calculated as energetically minima structures by DFT methods.



**Figure 10.** Molecular structure of **4.2-B**; adapted from ref 132. Hydrogen atoms are omitted for clarity.

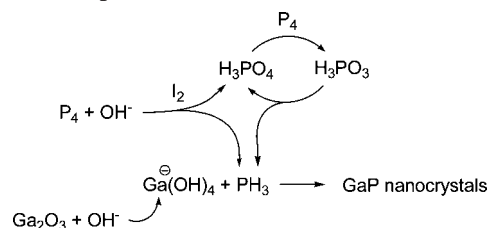


**Figure 11.** Molecular structure of  $[P_4Ga_3\{C(SiMe_3)_3\}_3]$  (**4.2-C**); adapted from ref 133. Hydrogen atoms are omitted for clarity.

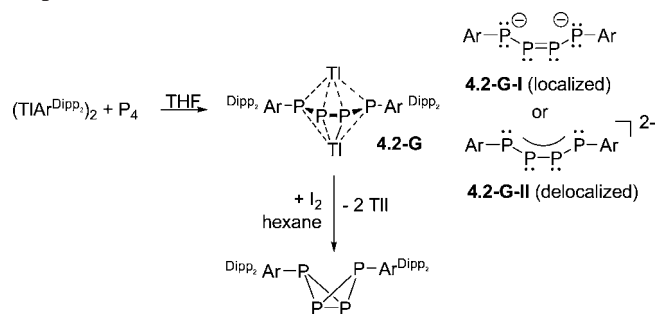
bonds to form the nortricyclane-like molecule **4.2-C**.<sup>133</sup> The solid-state structure is confirmed by X-ray diffraction analysis (Figure 11). However, in solution an unusual <sup>31</sup>P NMR shift of  $-521.9$  ppm is found for the apical P atom whereas the basal P atoms show an expected resonance at  $-202.8$  ppm. Also in **4.2-C** an oxidative addition reaction leading to Ga(III) moieties is discussed. In contrast to these redox reactions, starting from monovalent group 13 element compounds, Barron et al. found that the Lewis-acidic Ga(III) compound *t*Bu<sub>3</sub>Ga reacts with P<sub>4</sub> under insertion into a Ga–C bond and one P atom coordinates additionally to a Ga*t*Bu<sub>2</sub> moiety.<sup>134</sup> The obtained butterfly bridged molecule **4.2-D** (Figure 9) shows NMR data similar to structurally related transition metal substituted ML<sub>n</sub>(η<sup>2</sup>-P<sub>4</sub>) compounds.<sup>135</sup> However, from an electronic point of view it is more related to R<sub>2</sub>P<sub>2</sub>(P<sub>2</sub>) compounds (cf.: Figure 5 as an example) in which the electron deficient R<sub>2</sub>Ga species is bridged by the coordination of the lone pair of the *t*BuP moiety.

Another interesting molecule, **4.2-E**, is verified by the thermodynamic calculations of Schnöckel et al., when they investigated the transport reaction of Ga or In and phosphorus (using red phosphorus as starting material) to give the highly pure binary phases GaP and InP, respectively.<sup>136</sup> By DFT calculations, the stability of the C<sub>5v</sub> symmetric molecule **4.2-E** as well as the C<sub>s</sub> symmetric EP<sub>3</sub> molecule **4.2-F** (Figure 9) is shown and identified as an important gas phase species. In this context, Gao et al. report about an aqueous synthesis of well crystallized 13/15 semiconductors GaP and InP<sup>137</sup> by dismutation of white phosphorus in alkali solutions. The yield of PH<sub>3</sub> is increased by addition of iodine, and it reacts with E(OH)<sub>4</sub><sup>−</sup> (E = Ga, In), obtained from E<sub>2</sub>O<sub>3</sub>, to yield, e.g., GaP in these basic solutions (Scheme 3). Moreover, the preparation of nanocrystalline InP is reported by the reduction of InCl<sub>3</sub> with KBH<sub>4</sub> in the presence of P<sub>4</sub> phosphorus in ethylenediamine at 80–160 °C.<sup>138</sup>

**Scheme 3.** Reaction Cycle of the Formation of GaP from P<sub>4</sub> and Ga<sub>2</sub>O<sub>3</sub> (Adapted from Ref 137)



**Scheme 4.** Synthesis and Subsequent Oxidation of the Tl Compound **4.2-G** and Its Electronic Bonding Situations Depicted as **4.2-G-I** and **4.2-G-II**



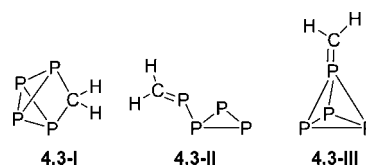
The group of Power introduced sterically crowded terphenyl substituents to stabilize unusual species and bonding situations. The reaction of the weakly dimerized dithallene (TlPh<sup>Dipp2</sup>)<sub>2</sub> (Ph<sup>Dipp2</sup> = C<sub>6</sub>H<sub>3</sub>-2,6-(C<sub>6</sub>H<sub>3</sub>-2,6-*i*Pr<sub>2</sub>)<sub>2</sub>) with P<sub>4</sub> phosphorus yields the thallium salt of the diaryl tetraphosphabutadienediide **4.2-G**.<sup>139</sup> The subsequent two electron oxidation with I<sub>2</sub> leads to the neutral diaryltetraphosphabicyclobutane P<sub>4</sub>(Ph<sup>Dipp2</sup>)<sub>2</sub> (Scheme 4), which is found to crystallize as the *trans,trans* and the *cis,trans* conformers depending on the solvent used. The X-ray structure of **4.2-G** reveals almost equal distances of the P–P bonds within the P<sub>4</sub> chain (2.136(4) for the *exo* and 2.143(6) Å for the *endo* P–P bonds). Thus, the bonding situation is interpreted to be rather delocalized (Scheme 4).

Moreover, it should be mentioned that the reaction of (C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>TlBr under thermal conditions (190 °C, sealed tubes) with P<sub>4</sub> phosphorus is reported, which results in (C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>P in 70% yield.<sup>140</sup>

### 4.3. Activation and Degradation of P<sub>4</sub> Phosphorus by Group 14 Element Compounds

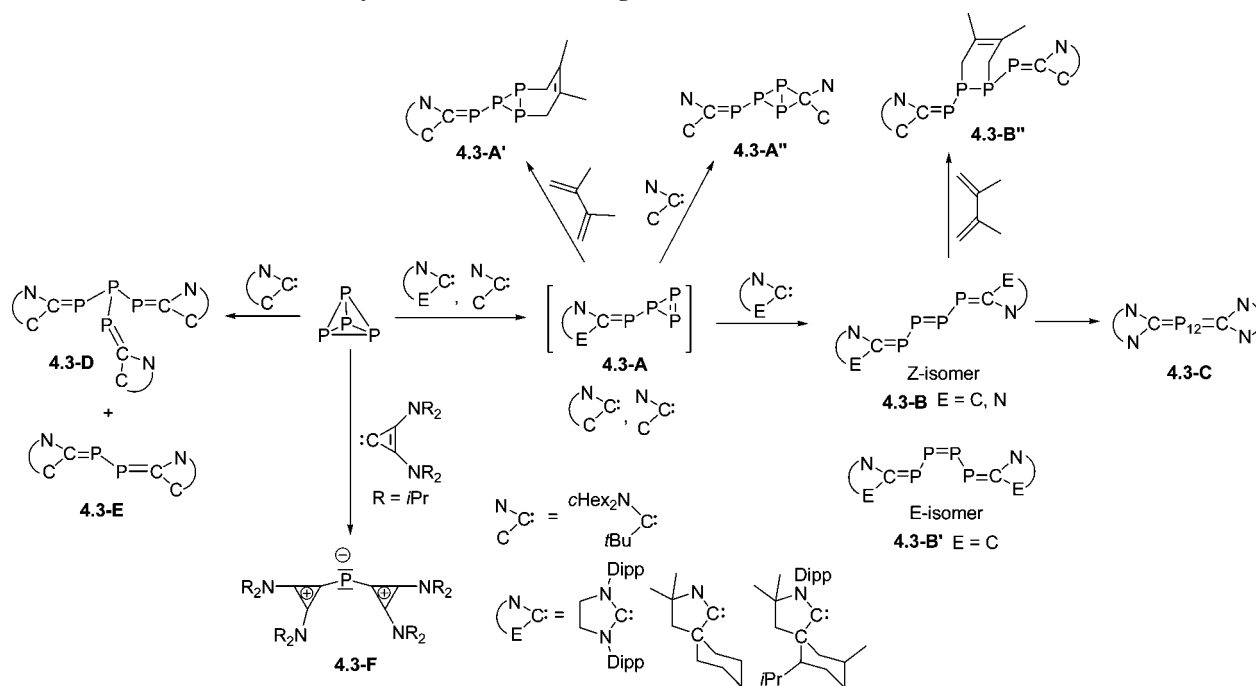
Recently, the activation of P<sub>4</sub> phosphorus by carbenes became a very active research area in which a large number of novel and interesting derivatives have been obtained. According to theoretical calculations, the parent triplet carbene CH<sub>2</sub> does not significantly interact with P<sub>4</sub>,<sup>141</sup> whereas for singlet methylene three energetic minima have been calculated by applying DFT methods (Figure 12).

The species of lowest energy is clearly **4.3-I** with a side-on P–P edge inserted carbene, followed by the [triangle+1]-



**Figure 12.** Calculated local energy minima structures of the reaction products of singlet CH<sub>2</sub> with P<sub>4</sub>; adapted from ref 141.



Scheme 5. Different Reaction Pathways of the Reaction of Singlet Carbenes with P<sub>4</sub>

structure **4.3-II** (+134 kJ mol<sup>-1</sup> higher in energy than **4.3-I**), containing a H<sub>2</sub>C=P moiety bound at a triphosphirene ring. Structure **4.3-III** is 172 kJ mol<sup>-1</sup> higher in energy than **4.3-I** and represents the situation of a first attack of the singlet carbene at a P<sub>4</sub> apex. The calculated P–C bond length of 1.68 Å in **4.3-III** is close to an expected C=P double bond, as is also found in **4.3-II** with 1.67 Å. The last structure most likely represents the first step of P<sub>4</sub> activation by stable singlet carbenes, for which Bertrand and co-workers find experimentally a variety of carbene compounds similar in structure to **4.3-II** as initial products of the reactions with P<sub>4</sub>.<sup>142</sup> This first proposed product **4.3-A** of such reactions is trapped by 2,3-dimethylbutadiene or a second equivalent of a carbene to give the isolated and structurally characterized derivatives **4.3-A'**<sup>143</sup> and **4.3-A''**<sup>142</sup> (Scheme 5). After rearrangement of **4.3-A**, the tetraphosphatrienes are detected as *Z*- (**4.3-B**; Figure 13) and *E*-isomers and **4.3-B'** and are crystallographically proven for some carbenes. Additionally, **4.3-B** is trapped by 2,3-dimethylbutadiene to give compound **4.3-B''**, which is characterized by X-ray diffraction.<sup>143</sup> The subsequent reaction is strongly dependent on the carbene used. While NHC carbenes are less basic and, therefore, better leaving groups and favor the P<sub>n</sub> cage formation reaction, by [3+2] cycloaddition reactions of **4.3-A** and **4.3-B**, intermediate **4.3-IV** is formed according to DFT calculations using the parent NHC (Scheme 6).<sup>144</sup> The release of the NHC, rearrangement to a heptaphosphanorbornene species **4.3-V**, and subsequent [π<sup>2</sup>+π<sup>2</sup>+π<sup>2</sup>] reaction with another triphosphirene molecule **4.3-A** without any energy barrier leads to the formation of a P<sub>12</sub> cluster **4.3-C**, the largest

neutral P<sub>n</sub> aggregate so far stabilized by main group element compounds (Figure 14).<sup>144</sup>

In contrast, by using a strongly basic but electrophilic carbene such as the acyclic alkyl-aminocarbene, which is one of the most electrophilically stable carbenes known, the [triangle+1]-form **4.3-A''** of P<sub>4</sub> could be stabilized and comprehensively characterized by NMR and X-ray (Scheme 5).<sup>142</sup> Here no rearrangement and leaving of the carbene is observed. In contrast, by using cyclic alkyl-aminocarbenes (CAAC's), the fragmentation of P<sub>4</sub> is induced, leading to the structurally characterized *iso*-tetraphosphine derivatives **4.3-D** (Figure 15) and the diphosphine product **4.3-E** (Figure 16). Whereas the former product is a formal 6e<sup>-</sup> reduction

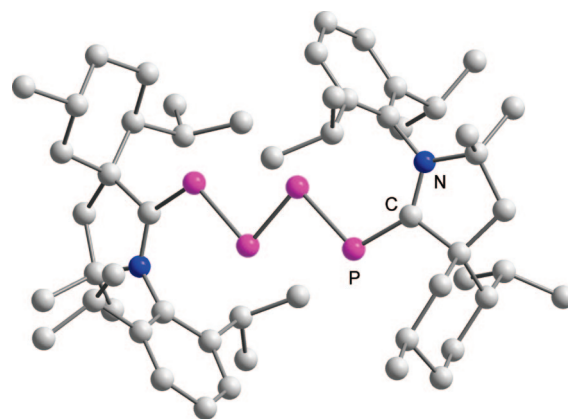
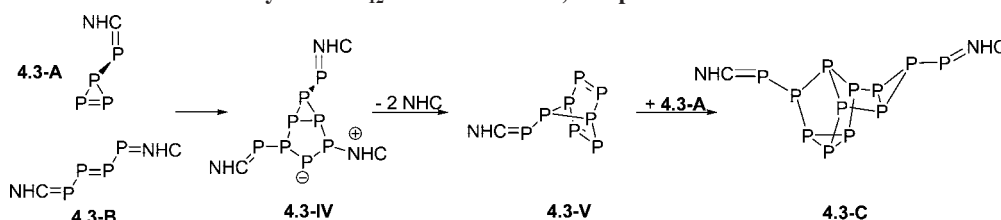
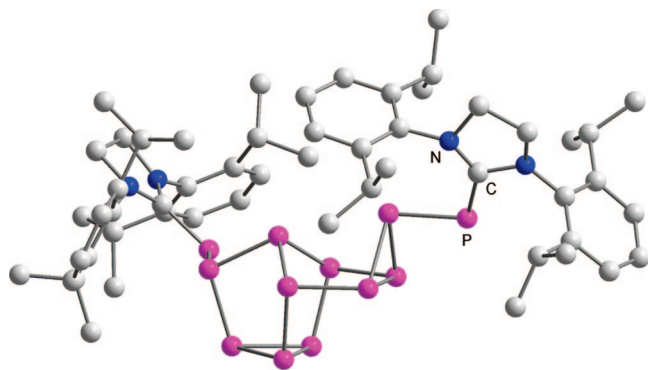
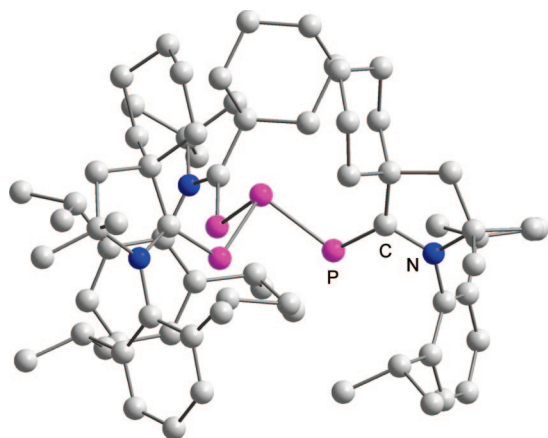


Figure 13. Molecular structure of the *Z*-isomer **4.3-B**; adapted from ref 143. Hydrogen atoms are omitted for clarity.

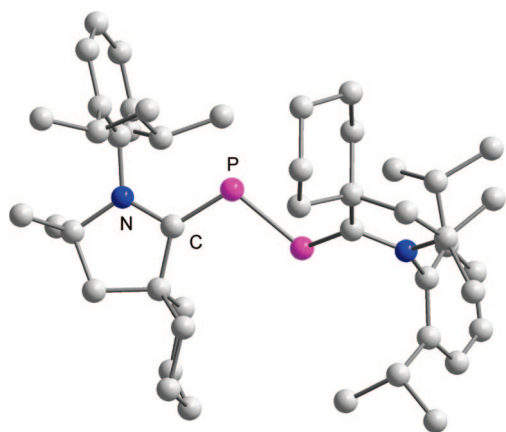
Scheme 6. Postulated Formation Pathway of the P<sub>12</sub> Derivative **4.3-C**, Adapted from Ref 144



**Figure 14.** Molecular structure of **4.3-C**; adapted from ref 144. Hydrogen atoms are omitted for clarity.



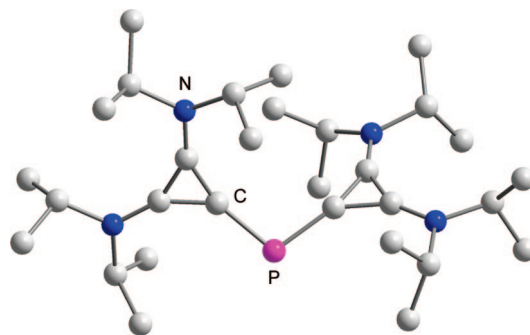
**Figure 15.** Molecular structure of **4.3-D**; adapted from ref 142. Hydrogen atoms are omitted for clarity.



**Figure 16.** Molecular structure of **4.3-E**; adapted from ref 142. Hydrogen atoms are omitted for clarity.

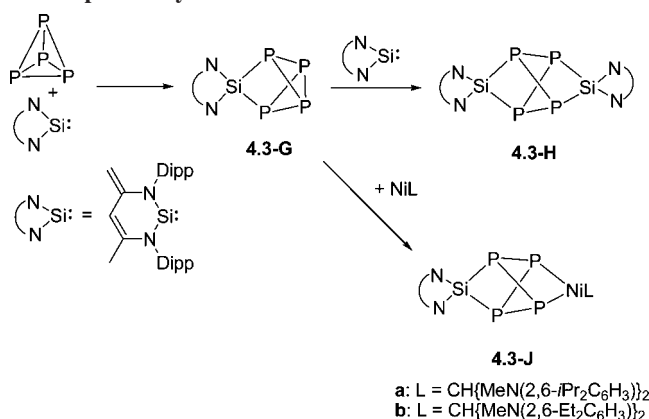
product of  $P_4$  phosphorus, the latter compound is reminiscent of a 2,3-diphosphabutadiene<sup>145</sup> and the NHC stabilized bis(phosphinidene) (Scheme 5).<sup>146</sup>

Electronic differences between CAAC's and NHC's lie in the smaller singlet–triplet gap, and the HOMO is higher in energy for the CAAC's.<sup>8</sup> Therefore, CAAC's may act as both better nucleophiles and electrophiles. This observed  $P_4$  fragmentation is completed by using the least sterically demanding, stable carbene known to date, namely bis(diisopropylamino)cyclopropylidene.<sup>142</sup> The corresponding reaction with  $P_4$  leads to the bis(carbene)  $P_1$  cation **4.3-F**, which is isolated from  $CHCl_3$  solutions as the  $Cl^-$  salt and the structure is determined by X-ray diffraction (Figure 17). **4.3-F** displays a high field  $^{31}P$  NMR resonance at  $-93.2$  ppm,



**Figure 17.** Molecular structure of the cation **4.3-F**; adapted from ref 142. Hydrogen atoms are omitted for clarity.

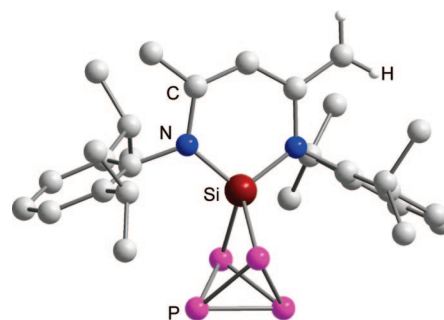
#### Scheme 7. Reaction Pathway of the Activation of $P_4$ by an Electrophilic Silylene



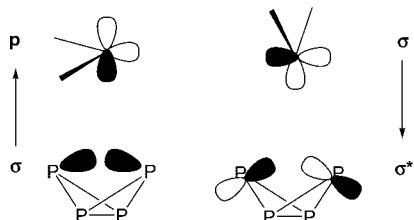
and the additionally determined ABX spin system for a probable  $P_3^-$  derivative shows the expected degradation of  $P_4$  into a  $P_1$  and  $P_3$  moiety. However, the latter  $P_3^-$  product decomposes readily upon workup of the reaction mixture.<sup>142</sup>

The big impact of  $P_4$  activation and degradation by carbenes is accompanied by the successful use of silylenes. In 1998, West et al. reported that NHC analogues of silylenes react with  $P_4$  to form, presumably, red phosphorus.<sup>147</sup> In contrast, the six-membered electrophilic silylene developed in the Driess group reacts with  $P_4$  phosphorus under subsequent opening of one and two P–P bonds (Scheme 7).<sup>148</sup> The first formed bicyclopentaphosphine derivative **4.3-G** possesses a tricyclo[3.1.0]pentane-like core (Figure 18). Such structural motifs are well-known from the transition metal chemistry in  $L_nM(\eta^2-P_4)$ .<sup>135</sup>

Interestingly, this structural moiety (Figure 18) is also the most stable local energy minimum of a one-to-one species of the interaction of singlet parent silylene,  $SiH_2$ , with  $P_4$ .<sup>149</sup> Here, calculated by DFT methods, similar species to **4.3-I–4.3-III** (Figure 12) are found, as for the singlet parent

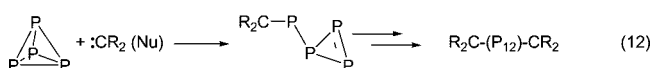
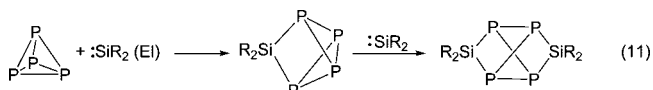


**Figure 18.** Molecular structure of **4.3-G**; adapted from ref 148. Some hydrogen atoms are omitted for clarity.

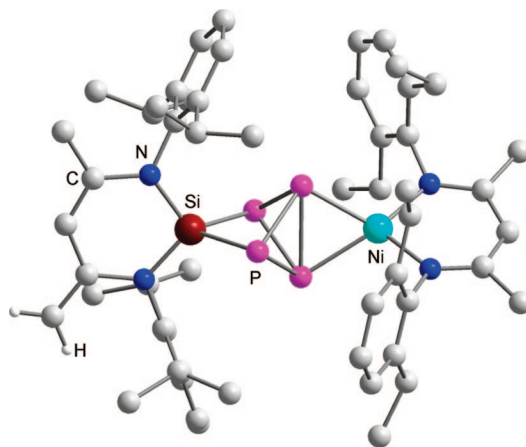
**Scheme 8. Schematic Nucleophilic and Electrophilic Attack of a Carbene-like Species at a P–P Edge of the P<sub>4</sub> Tetrahedron**


carbene CH<sub>2</sub>. In addition, different migrated H isomers are also determined, among them a noncovalent linked SiH<sub>2</sub> to the P<sub>4</sub> molecule, revealing a bond energy of ~23.0 kJ mol<sup>-1</sup>.<sup>149</sup> The monosubstituted derivative **4.3-G** reacts with another molecule of the silylene to open the opposite P–P bond to form **4.3-H**, containing a *cyclo*-tetraphosphorus unit (asterane-shaped P<sub>4</sub> core; Scheme 7). The P–P bond lengths are somewhat longer than those in the starting material (**4.3-G**: 2.229(2) Å (av); **4.3-H**: 2.285(1) Å (av)). The stepwise reaction sequence in the case of the silylene is different from the spontaneous multiple insertion of subvalent carbene—analogue to the group 13 elements.

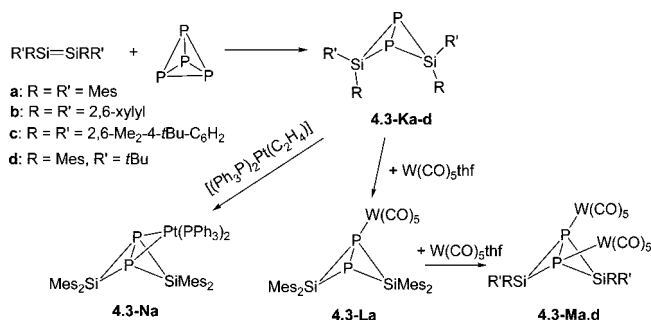
The differences between the reactivity of carbenes and silylenes are significant. Recent theoretical studies<sup>150</sup> show that the major reasons lie in the predominant nucleophilic reactivity of the carbenes, in comparison to the case of the more electrophilic silylene of the Driess group. In Scheme 8 the electrophilic as well as the nucleophilic attack of a carbene-like species at the  $\sigma$  or the  $\sigma^*$  orbital of a P–P edge of the P<sub>4</sub> is schematically shown. This behavior is much more pronounced for more electrophilic silylenes, to result, first, in an edge opening at the P<sub>4</sub> phosphorus, as shown in eq 11. As shown by corresponding calculations of the transition state, the energy of this side-on attack is lowered by participation of a second molecule P<sub>4</sub> in a trigonal bipyramidal arrangement at the silicon center. This autocatalytic effect of P<sub>4</sub> is not possible for carbenes, because the lone pairs are more nucleophilic and prefer a nucleophilic attack at an apex of the P<sub>4</sub>. Here, a triphosphirene compound is first formed and subsequent cycloaddition reactions with other species lead to polyphosphorus species (eq 12).<sup>150</sup> It has not yet been calculated if this kind of interaction is also true for carbene-like compounds of group 13 elements. However, as the results for cationic phosphonium compounds show (section 4.4), the side-on attack by electrophiles is, hereby, the dominating reaction pathway.



Moreover, the silaphosphorus compound **4.3-G** serves in further reactions. With transition metal compounds such as the  $\beta$ -diketimatonickel(I) complex [(L'Ni)<sub>2</sub>•toluene] (L' = CH{CMeN(2,6-R<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)<sub>2</sub>; R = *i*Pr, Et), heterobinuclear tetraphosphorus complexes **4.3-J** (Scheme 7) with a Si( $\mu$ , $\eta$ <sup>2:2</sup>-P<sub>4</sub>)Ni core are obtained and structurally confirmed by X-ray diffraction (Figure 19).<sup>151</sup> In contrast to the bisilylene derivative **4.3-H**, the second P–P bond is not opened. This P–P distance is 2.335(4) Å (**4.3-Ja**) and



**Figure 19.** Molecular structure of **4.3-Jb**; adapted from ref 151. Some hydrogen atoms are omitted for clarity.

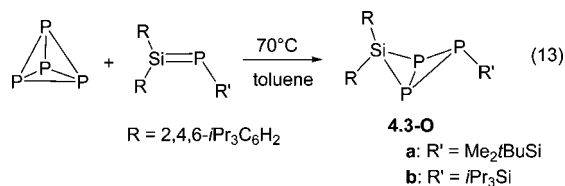
**Scheme 9. Reactivity of P<sub>4</sub> with a Disilene and Subsequent Reactions**


2.351(3)/2.354(2) Å (two independent molecules in **4.3-Jb**) and, therefore, still in the range of a P–P bond interaction. EPR measurements confirm the existence of Ni(I) centers. Thus, these derivatives represent rare examples of heterobinuclear tetraphosphorus complexes with different stages of P–P bond activation.

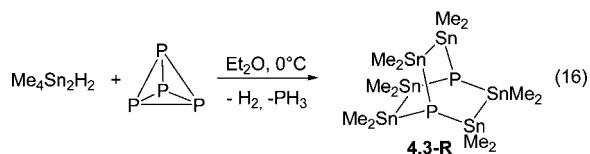
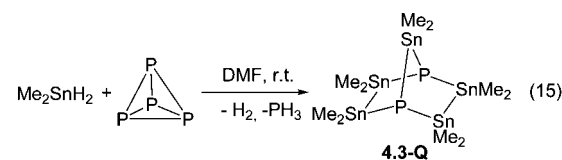
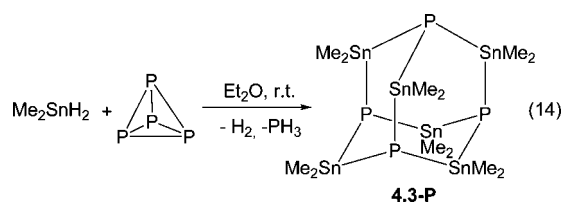
Also, Si=Si double bond compounds are able to activate P<sub>4</sub> phosphorus. The reaction of disilenes with P<sub>4</sub> in toluene at 40 °C leads to the formation of 1,3-diphospha-2,4-disilabicyclo[1.1.0]butanes (**4.3-Ka-d**), the structure of which is confirmed by heteroelement NMR and mass spectroscopic methods (Scheme 9).<sup>152</sup> For the Mes/*t*Bu derivative of the disilene at that temperature, a stable intermediate Mes<sub>4</sub>(*t*Bu)<sub>4</sub>Si<sub>2</sub>P<sub>4</sub> was isolated, and by <sup>31</sup>P NMR characterization, two possible isomeric structures could be proposed.<sup>152b</sup> Interestingly, by using a P<sub>4</sub> free approach, the X-ray structure of **4.3-Kd** was determined.<sup>152c</sup> The following reaction of the 1,3-diphospha-2,4-disilabicyclo[1.1.0]butane **4.3-Ka** with W(CO)<sub>5</sub>THF leads to a stepwise coordination of the P lone pairs to the Lewis acidic units and the isolation of **4.3-La** and **4.3-Ma**, respectively. Moreover, with Pt(0) complexes such as [(Ph<sub>3</sub>P)<sub>2</sub>Pt(C<sub>2</sub>H<sub>4</sub>)], the propellane-like derivative **4.3-Na** is isolated. All these derivatives are spectroscopically characterized. Additionally, the structures of **4.3-Ma** and **d** are confirmed by X-ray crystallography.<sup>152a,b</sup>

In an analogous approach, P<sub>4</sub> is reacted with a stable phosphasilene containing a silicon–phosphorus double bond<sup>153</sup> stabilized by bulky substituents which enable the starting material to react at 70 °C in toluene. As a result, 1,2,3-triphospha-4-silabicyclo[1.1.0]butanes **4.3-Oa,b** are isolated as the *exo* diastereomers (eq 13). The products are characterized by NMR spectroscopy and mass spectrometry, revealing the expected data for a bicyclic compound.





Tetraphenyltin reacts with  $\text{P}_4$  phosphorus in a sealed tube above  $220^\circ\text{C}$  to form  $\text{Ph}_3\text{P}$  and alloy-like tin phosphides.<sup>154</sup> In contrast, an interesting reaction behavior of  $\text{P}_4$  is found in the reaction with dimethyl-tin-dihydride.<sup>155</sup> Depending on the solvents used, it reacts under  $\text{PH}_3$  elimination to form  $(\text{Me}_2\text{Sn})_6\text{P}_4$  (**4.3-P**) with an adamantane-like core (eq 14) or  $(\text{Me}_2\text{Sn})_5\text{P}_2$  (**4.3-Q**) with a norbornane-like structure (eq 15). A more tin-rich product, the 1,4-diphospha-2,3,5,6,7,8-hexastannabicyclo[2.2.2]octane **4.3-R** is formed if a corresponding distannanehydride is used in the reaction with  $\text{P}_4$  (eq 16).<sup>156</sup>



By treatment of  $\text{SnCl}_2$  with  $\text{KBH}_4$  in the presence of  $\text{P}_4$  phosphorus under hydrothermal conditions (EtOH,  $160^\circ\text{C}$ , autoclave, 10 h), the synthesis of a compound with the composition  $\text{Sn}_4\text{P}_3$  is reported.<sup>157</sup> As a possible mechanism, the reduction to atomic Sn and subsequent reaction with  $\text{P}_4$  to  $\text{Sn}_4\text{P}_3$  is proposed.

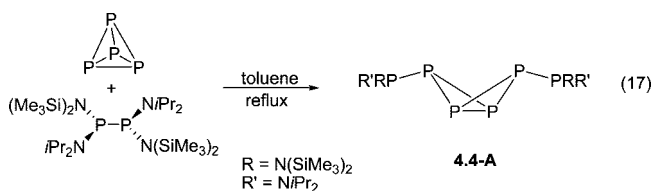
The reaction of  $\text{P}_4$  phosphorus with benzaldehyde in  $\text{H}_3\text{PO}_4$  under KI catalysis is reported to give an isophosphindoline derivative, L-phenyl-1,3-dihydro-2 $\lambda^5$ -benzophosphonic acid.<sup>158</sup> As a reaction pathway, the conversion of  $\text{P}_4$  into  $\text{H}_3\text{PO}_2$  is proposed, which, with 2 mols of benzaldehyde, forms bis( $\alpha$ -hydroxybenzyl)phosphinic acid in a kind of heteroaldol condensation. The subsequent protonation and cleavage of  $\text{H}_2\text{O}$  leads to a benzylic carbenium ion which, by intramolecular Friedel-Crafts alkylation of the other benzyl ring, finally affects ring closure to form the benzophosphonic acid.

Remarkable host-guest chemistry is found when  $\text{P}_4$  phosphorus is encapsulated in a self-assembled tetrahedral capsule.<sup>159</sup> The advantage of this host-guest complex is the air stability and water solubility. By adding stronger guests, such as, e.g., benzene,  $\text{P}_4$  is completely released into the benzene solution. Latter exposure to air causes quantitative transformation into phosphoric acid. Another example of host-guest chemistry of molecular  $\text{P}_4$  is found when a solution of  $\text{C}_{60}$  is treated with  $\text{P}_4$ .<sup>160</sup> The formed compound has the composition  $(\text{P}_4)_2\text{C}_{60}$ , and the structure is determined

by XPD measurements and solved by Rietveld refinement. The analysis suggests an AAA stacking of closed packed  $\text{C}_{60}$  layers with tetrahedral  $\text{P}_4$  units between them. The  $^{31}\text{P}$  MAS and  $^{13}\text{C}$  MAS data of the crystalline black-blue solid are interpreted as meaning that no charge transfer has occurred.

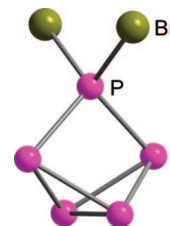
#### 4.4. Activation and Degradation of $\text{P}_4$ Phosphorus by Group 15 Element Compounds

Compounds of the type  $\text{R}_2\text{E}^-$  ( $\text{E} = \text{N}, \text{P}$ ) are good nucleophiles and are broadly used for the nucleophilic  $\text{P}_4$  degradation reaction which is discussed in section 3.2. Interestingly,  $\text{P}_4$  phosphorus induces an oxidative C-C coupling reaction when it is reacted with (2-pyridylmethyl)-(trialkylsilyl)amide, leading to  $\text{P}_7^{3-}$  as a phosphorus containing product among 1,2-dipyridyl-1,2-bis(*tert*-butyldimethylsilylamido)ethane.<sup>161</sup>



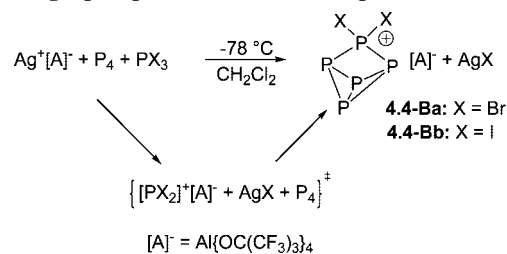
Another interesting behavior with  $\text{P}_4$  is reported by the Lappert group when a sterically encumbered diphosphine  $[\text{P}\{\text{N}(\text{SiMe}_3)_2\}(\text{NiPr}_2)]_2$  is used as starting material.<sup>162</sup> ESR measurements show that in *n*-hexane solutions of the starting material a reversible dissociation occurs. Subsequent reaction with  $\text{P}_4$  gives the diphosphanyl-bicycletetraphosphine derivative **4.4-A** as a mixture of *meso*- and *rac*-diastereomers (eq 17).

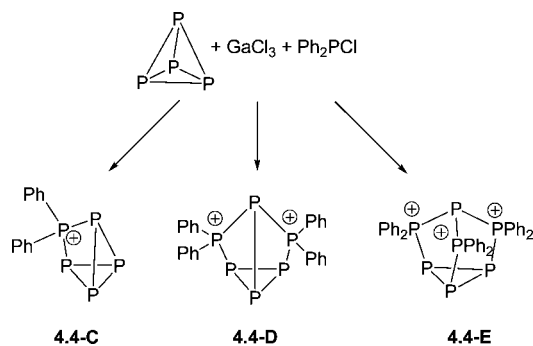
From the metathesis of the Ag salt  $\text{Ag}[\text{Al}\{\text{OC}(\text{CF}_3)_3\}_4]$  with  $\text{PX}_3$  ( $\text{X} = \text{Br}, \text{I}$ ), presumably  $\text{PX}_2^+$  cations arise that act as electrophilic carbene analogues and insert into the P-P bond of the  $\text{P}_4$  tetrahedron (Scheme 10).<sup>163</sup> By this method, the novel  $\text{C}_{2v}$  symmetric  $\text{P}_5$  cages **4.4-Ba,b** are synthesized, the Br derivative of which is structurally characterized (Figure 20).<sup>164</sup> The quantitatively formed products are stable under inert atmosphere at  $-30^\circ\text{C}$  for months and are



**Figure 20.** Molecular structure of the cation  $[\text{P}_5\text{Br}_2]^+$  (**4.4-Bb**<sup>+</sup>), adapted from ref 163.

#### Scheme 10. Reaction of $\text{P}_4$ Phosphorus with $\text{PX}_3$ in the Presence of a Silver Salt and the Proposed Intermediate of the Dihalogenphosphenium Cation (Adapted from Ref 163)

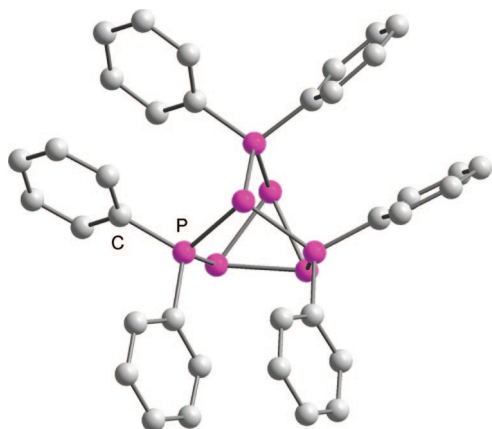


**Scheme 11. Multiple Insertion Reaction of a Phosphenium Cation into P–P Bonds of the P<sub>4</sub> Tetrahedron**


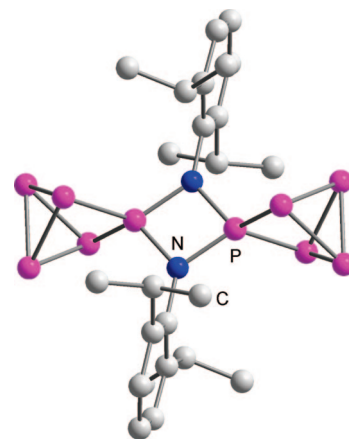
analyzed by Raman spectroscopy. Variable temperature <sup>31</sup>P NMR spectroscopy in solution shows no dynamic behavior, so the rigid C<sub>2v</sub> symmetry of the solid-state is maintained in solution.

The formation of the PX<sub>2</sub><sup>+</sup> salt is limited at low temperatures for which the insertion in only one P–P bond is observed, confirming the reaction behavior of electrophilic carbene-like molecules, as already discussed for silylenes (cf. section 4.3). In contrast, diorganylphosphonium cations are much more stable and, therefore, valuable for use at higher temperatures. That opens more possibilities for multiple P–P bond insertion into the P<sub>4</sub> molecule. Following an established method to generate Ph<sub>2</sub>P<sup>+</sup> cations<sup>165</sup> from Ph<sub>2</sub>PCl and GaCl<sub>3</sub> depending on the stoichiometry and reaction temperatures (60–100 °C), Weigand et al. succeeded in the formation and characterization of the mono-, di-, and trifold inserted P<sub>4</sub> products **4.4-C**, **4.4-D**, and **4.4-E**, respectively (Scheme 11).<sup>166</sup> All products are comprehensively characterized by <sup>31</sup>P NMR spectroscopy, revealing no dynamic behavior at room temperature. **4.4-C**[GaCl<sub>4</sub>]<sup>−</sup> and **4.4-E**[Ga<sub>2</sub>Cl<sub>7</sub>]<sup>−</sup> are isolated in good yields and are very air and moisture sensitive. The X-ray structural characterization reveals the C<sub>2v</sub> symmetric cage of **4.4-C** is similar to that of **4.4-B** and the nortricyclane (tricyclo[2.2.1.0<sup>2,6</sup>]heptane) skeleton of **4.4-E** (Figure 21), reminiscent of the P<sub>7</sub><sup>3−</sup> anion or P<sub>4</sub>S<sub>3</sub>. The 2-fold inserted product **4.4-D** is not isolated; however, it is characterized by <sup>31</sup>P NMR spectroscopy in the reaction mixture together with both other products.

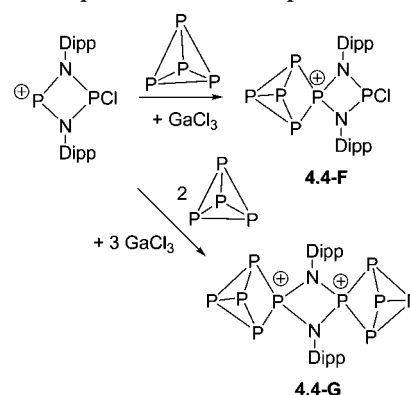
In continuation of these investigations, P<sub>4</sub> is reacted with an *in situ* formed monocation of the *cyclo*-1,3-diphospha-2,4-diazane [DippNPCI]<sub>2</sub> to give the monocationic compound **4.4-F** as the GaCl<sub>4</sub><sup>−</sup> salt (Scheme 12).<sup>167</sup> By adding an excess



**Figure 21.** Molecular structure of the trication **4.4-E**, adapted from ref 166. Hydrogen atoms are omitted for clarity.



**Figure 22.** Molecular structure of **4.4-G**, adapted from ref 167. Hydrogen atoms are omitted for clarity.

**Scheme 12. Monoinsertion and Double-Insertion of a Bifunctional Phosphenium Cationic Species into P<sub>4</sub>**


of the Lewis base GaCl<sub>3</sub> and 2 equiv of P<sub>4</sub>, the novel dicationic species **4.4-G** is formed, in which, according to the X-ray structure, two P<sub>4</sub> molecules are linked as P<sub>5</sub><sup>+</sup> moieties by imido bridges (Figure 22). Both products have been analyzed with their ambitious spin systems by <sup>31</sup>P NMR spectroscopy and by single crystal X-ray diffraction.

**4.5. Activation and Degradation of P<sub>4</sub> Phosphorus by Group 16 and 17 Element Compounds**

Oxidation of white phosphorus by molecular dioxygen leads to the P(III) and P(V) oxides P<sub>4</sub>O<sub>6</sub> and P<sub>4</sub>O<sub>10</sub>, from which the other phosphorus oxides P<sub>4</sub>O<sub>n</sub> (*n* = 6–10) are synthesized.<sup>1</sup> IR laser spectroscopic studies of the selective oxidation of P<sub>4</sub> vapor by O atoms reveal the suboxide P<sub>2</sub>O as an *in situ* gas phase species.<sup>168,169</sup> By this method, PO and PO<sub>2</sub> have also been detected.<sup>169</sup> In a more preparative approach at moist air, besides PO and PO<sub>2</sub> and finally phosphoric acid, O<sub>3</sub> was also detected and used to decompose toxic organic compounds.<sup>170</sup> By using ozone as an oxidant, P<sub>2</sub> molecules produced from P<sub>4</sub> react in a matrix to a series of P-oxides (PO, PO<sub>2</sub>, P<sub>2</sub>O, P<sub>2</sub>O<sub>2</sub>, P<sub>2</sub>O<sub>3</sub>, P<sub>2</sub>O<sub>4</sub>, and P<sub>2</sub>O<sub>5</sub>), among them the P<sub>4</sub>O molecule.<sup>171</sup> The latter species could be directly obtained by ozonolysis of P<sub>4</sub>.<sup>172</sup> Interestingly, oxygen–phosphorus systems reveal chemiluminescent properties.<sup>173</sup> Moreover, a series of multicomponent reactions of P<sub>4</sub> with oxygen and organic compounds, such as olefins,<sup>174</sup> phenols,<sup>175,176</sup> or alcohols,<sup>177</sup> are reported, leading to triorganylphosphate as the P containing product.

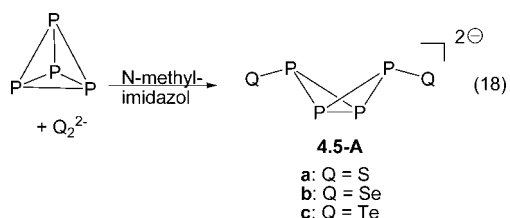
The melt between P, sulfur, and selenium, respectively, gives, e.g., the phosphorus sulfides  $P_4S_n$  ( $n = 2-10$ ) and the corresponding selenides.<sup>1,178</sup> Some mechanistic studies at low temperatures ( $<100$  °C) are reported on the reaction of  $P_4$  with  $S_8$ , giving evidence to the existence of a  $S_8$  diradical.<sup>179</sup>

Moreover,  $P_4$  phosphorus is degraded by nucleophiles such as  $^-OR$  and  $^-SR$ , as described in section 3.2. A series of reactions between  $P_4$  and  $S_8$  in the presence of  $H_2S$ <sup>180</sup> or directly by reaction of  $P_4$  with polysulfides<sup>181</sup> was reported to give different thiophosphates. NMR evidence for phosphorus-rich cages with  $P_5S_2$  and  $P_6S$  skeletons has been reported by the reaction of  $P_4$  with  $S_8$  and  $I_2$  in  $CS_2$  solutions.<sup>182</sup>

Catalytic amounts of hydroxide ions catalyze the reaction of  $P_4$  with RSSR via an ionic reaction mechanism to give  $(RS)_3P$ , whereas in the absence of  $HO^-$  the reaction proceeds at higher temperatures via a radical mechanism.<sup>183</sup>

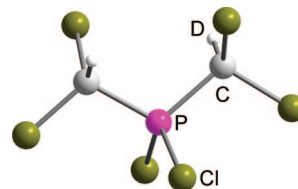
Depending on the reaction conditions, derivatives of hypophosphorous acid, phosphorous acid, mono- and diorgano hydrogen phosphonates, and phosphoric acid or triorganophosphates are produced by the oxidation of white phosphorus by hydrogen peroxide or different organic peroxides (such as *tert*-butyl hydroperoxide, dibenzoylperoxide, 3-chloroperoxybenzoic acid) in both aqueous and alcoholic solutions under anaerobic conditions.<sup>184</sup> The catalytic oxidative P–O coupling is accomplished by using Cu(I), Cu(II), and V(IV) complexes. A radical mechanism is suggested for both the stoichiometric and the catalytic oxidative hydroxylation, alkoxylation, and phenoxidation of  $P_4$  promoted by peroxides both under aqueous biphasic conditions and in organic solutions. The catalytic oxidative alkoxylation of  $P_4$  with oxygen were reported using Pd(II) and Ru(II) catalyst and a co-oxidant such as  $CuCl_2$ ,  $NaNO_2$ , or  $FeCl_3$ , leading to trialkylphosphates  $(RO)_3P(O)$  and dialkylphosphites  $(RO)_2P(O)H$ .<sup>185</sup>

More recently, Karaghiosoff et al. reacted  $P_4$  with the dichalcogen dianions  $Q_2^{2-}$  ( $Q = S, Se, Te$ ) in *N*-methylimidazole at ambient temperatures (eq 18).<sup>186</sup> According to the  $^{31}P$  NMR data, the dianions  $P_4Q_2^{2-}$  (**4.5-A**) are formed among some other byproducts, such as, e.g.,  $NaP_5$ , as the only detectable isomers, revealing a tetraphosphabicyclo-[1.1.0]butane butterfly-like structure with the chalcogen atoms in the sterically more favorable exo positions. Unexpectedly, the stability of the  $P_4Q_2^{2-}$  anions decreases from the tellurium to the sulfur derivative.

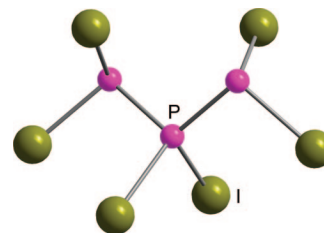


$P_4$  phosphorus is usually oxidized by halogens to form  $PX_3$  or  $PX_5$  derivatives. Some mixed phosphorus halides have been synthesized by the reaction of  $P_4$  with mixtures of halogens and characterized by NMR spectroscopy.<sup>187</sup>

Krossing et al. investigated the reaction of  $P_4$  with  $Br_2$  and  $I_2$  in the presence of the Ag salt  $Ag^+[A]^-$   $A^- = [Al\{OC(CF_3)_3\}_4]^-$  and proposed the formation of a  $P_5^+$  cation as an intermediate based on thermochemical calculations of Born–Haber cycles of different formation and decomposition



**Figure 23.** Molecular structure of the cation of **4.5-B**, adapted from ref 188.



**Figure 24.** Molecular structure of the cation of **4.5-C**, adapted from ref 188.

processes.<sup>188</sup> As products  $[Cl_2P^+(CDCl_2)_2][A^-]$  (**4.5-B**) and  $[P_3I_6]^+[A]^-$  (**4.5-C**) are isolated and structurally characterized by X-ray diffraction analysis. For **4.5-B** (Figure 23), the tetrahedral arrangement around the  $P^+$  cation is revealed, consisting of two Cl substituents and two C bound  $CDCl_2$  moieties, with the latter coming from  $CD_2Cl_2$ . The P–C bonds represent single bond distances (1.835(9) and 1.818(7) Å). The structure of  $[P_3I_6]^+$  (Figure 24), a first subvalent P-halogen cation, shows  $C_s$  symmetry with P–P and P–I bond lengths in the usual ranges. Moreover, DFT calculations on the proposed  $P_5^+$  cation give a  $C_{4v}$  symmetric square-pyramidal anion as the energetically most favored structure.

## 5. Abbreviations

18-crown-6	1,4,7,10,13,16-hexaoxacyclooctadecane ( $[-CH_2CH_2-O-]_6$ )
BCP	bond critical point
Bu	<i>n</i> -butyl ( $C_4H_9$ )
<i>t</i> Bu	<i>tert</i> -butyl ( $C_4H_9$ )
CBS	complete basis set
Cp*	pentamethylcyclopentadienyl ( $C_5Me_5$ )
CAAC	cyclic (alkyl)(amino)carbene
DFT	density functional theory
DME	dimethoxyethane
DMF	dimethylformamide
diglyme	diethyleneglycol dimethyl ether
Dipp	diisopropylphenyl ( $C_6H_3iPr_2-2,6$ )
en	ethylenediamine
EPR	electron paramagnetic resonance
Et	ethyl ( $C_2H_5$ )
Et <sub>2</sub> O	diethyl ether
HOMO	highest occupied molecular orbital
ICR	ion cyclotron resonance
M	metal
MAS	magic angle spinning
Me	methyl ( $CH_3$ )
Mes	mesityl ( $C_6H_2Me_3-2,4,6$ )
MO	molecular orbital
nacnac	$\beta$ -diketiminate
naph.	naphthalene
NHC	N-heterocyclic carbene
NMR	nuclear magnetic resonance
NR	neutralization–reionization
Ph	phenyl ( $C_6H_5$ )
Ph'	diisopropylphenyl ( $C_6H_3iPr_2-2,6$ )
ppm	parts per million



Pr	<i>n</i> -propyl (C <sub>3</sub> H <sub>7</sub> )
<i>i</i> Pr	isopropyl (C <sub>3</sub> H <sub>7</sub> )
SCF	self-consistent field
THF	tetrahydrofuran
Q	chalcogen
XPD	X-ray powder diffraction

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