

# Reductive Elimination at Pb(II) Center of an (Amino)plumbylene-Substituted Phosphaketene: New Pathway for Phosphinidene Synthesis

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**Abstract:** A stable (amino)plumbylene-substituted phosphaketene **3** was synthesized by the successive reactions of PbCl<sub>2</sub> with two anionic reagents (lithium amidophosphine and NaPCO). Of particular interest, the thermal evolution of **3**, at 80 °C, leads to the transient formation of corresponding amino- and phosphanylidene-phosphaketenes (**6** and **7**), via a

reductive elimination at the Pb<sup>II</sup> center forming new N–P and P–P bonds. Further evolution of **6** gives a new cyclic (amino)phosphanylidene phosphorane **4**, which shows a unique reactivity as a phosphinidene. This result provides a new synthetic route to phosphinidenes, extending and facilitating further their access.

## Introduction

Since the first discovery of [PCO][Li] as an isolable salt by Becker et al. in 1992<sup>[1]</sup> as well as the synthesis of the remarkably stable [(dioxane)<sub>n</sub>Na][PCO] salt by Grützmacher et al.<sup>[2]</sup> in 2011 and the [(18-crown-6)K][PCO] salt by Goicoechea et al. in 2013,<sup>[3]</sup> the 2-phosphaethynolate anion (PCO<sup>−</sup>) has been recognized as a useful nucleophilic reagent to conveniently introduce the PCO unit into various molecules.<sup>[4,5]</sup> Due to the labile nature of

phosphaketene function, the resulting molecules (E–P=C=O) I readily release CO by photolysis or thermolysis and, thus, can be used as efficient precursors of reactive phosphinidenes with only CO gas as byproduct (Figure 1).<sup>[6]</sup> Therefore, this methodology is one of the most convenient routes for the synthesis of phosphinidenes.<sup>[7]</sup> Using this methodology, Bertrand et al. successfully synthesized the first stable singlet (phosphino)-phosphinidene II.<sup>[8]</sup> The particularly strong electrophilic character of II was demonstrated by the formation of adducts III with

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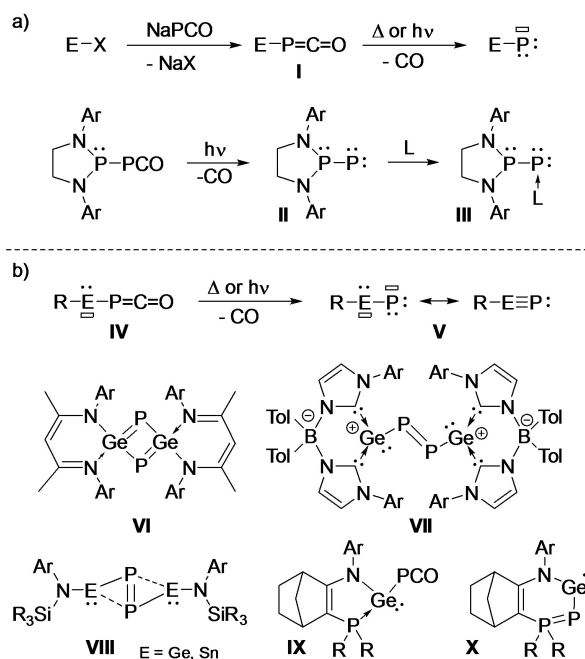
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**Figure 1.** a) Synthesis and CO elimination of E-PCO. b) Metallylene-substituted PCO species.

various Lewis bases, even with (This line break should be cancelled. I can not cancel it by myself.–>) CO,<sup>[9]</sup> implying the difficulty of such a synthesis by other methods. Phosphaketenes **IV** bound to a divalent element of group 14, should also readily lose CO to generate the corresponding heavier phosphalkyne derivatives **V**. Although the appropriate model for accessing stable heavier phosphalkynes remains elusive, this methodology has enabled the synthesis of a series of unexpected new phosphorus compounds (**VI–VIII**).<sup>[10]</sup> We also reported the thermolysis of phosphine-stabilized germylene-PCO species **IX**, as a precursor of an original N,P-heterocyclic germylene **X**.<sup>[11]</sup> Despite the high synthetic potential of metallylene-substituted phosphaketenes **IV**, the variation of such compounds is still limited and, to our knowledge, only germylene and stannylene derivatives (E=Ge, Sn) have been described to date.

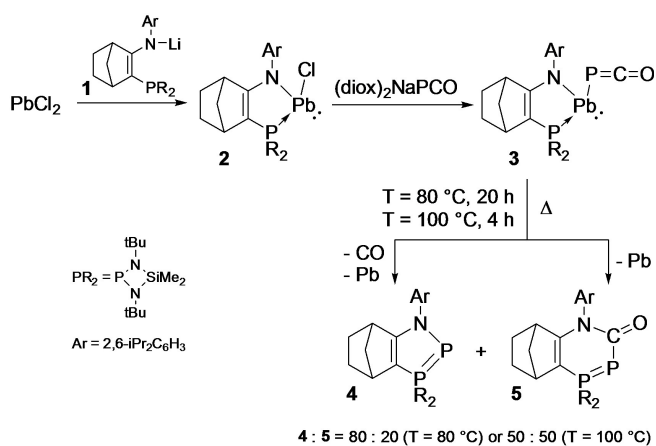
Here we report the synthesis of a novel phosphaketene-substituted plumbylene **3** intramolecularly stabilized by a phosphine ligand. Unlike the lighter analogues, a reductive elimination at Pb<sup>II</sup> center of **3** affords a cyclic (amino)phosphanylidene- $\sigma^4$ -phosphorane **4** that exhibits a unique reactivity as an imine-stabilized phosphinidene. This result provides a new synthetic route to phosphinidenes, extending and facilitating further their access.

## Results and Discussion

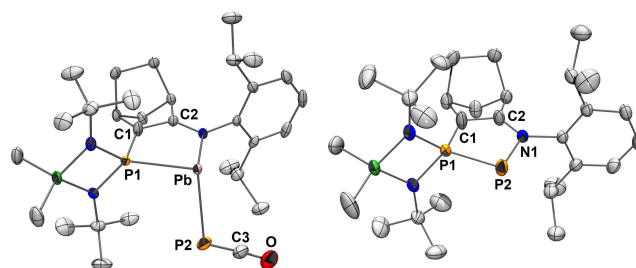
The phosphaketene-substituted plumbylene **3** was synthesized by the successive reactions of PbCl<sub>2</sub> with two anionic reagents such as the amidophosphine **1** to form the phosphine-stabilized chloro(amino)-plumbylene **2** and then the sodium phosphae-thynolate (Scheme 1).<sup>[2]</sup> The phosphaketene **3** was isolated as yellow crystals in good yield (71%). Phosphaketene **3** was obtained as a mixture of two diastereomers (55:45) as indicated, in the <sup>31</sup>P NMR spectrum, by two sets of singlet signals that show satellites due to coupling with <sup>207</sup>Pb, corresponding to the phosphine ligand (major isomer:  $\delta = 182.3$  ppm,  $^1J_{\text{PbP}} = 3688$  Hz, minor isomer:  $\delta = 189.2$  ppm,  $^1J_{\text{PbP}} =$

3799 Hz) and to the phosphaketene fragment (major isomer:  $\delta = -333.2$  ppm,  $^1J_{\text{PbP}} = 945$  Hz, minor isomer:  $\delta = -329.4$  ppm,  $^1J_{\text{PbP}} = 976$  Hz). The two <sup>207</sup>Pb NMR signals observed at 2460 ppm (major isomer) and 2233 ppm (minor isomer) appear as two doublets of doublets with the same coupling constants observed in <sup>31</sup>P NMR. The structure of **3** was unambiguously confirmed by an X-ray diffraction analysis (Figure 2-left).<sup>[12]</sup> The molecular structure of **3** exhibiting a strongly pyramidalized Pb center ( $\Sigma \sigma_{\text{Pb}}^+ = 268.07^\circ$ ) and an acute Pb–P2–C3 angle [87.3(3)°], is similar to the previously reported structures of germylene analogues **IX** [Ge–P–C 86.01(12)].<sup>[11]</sup>

Phosphaketene **3** is thermally unstable, and starts to evolve around 80 °C in toluene. Monitored by <sup>31</sup>P NMR spectroscopy, the complete disappearance of **3** was observed after 20 h at 80 °C or 4 h at 100 °C. Contrary to the other cases, metallic lead precipitates as a black powder during the reaction, leading to the formation of two cyclic phosphanylidene- $\sigma^4$ -phosphoranes **4** and **5** (Scheme 1).<sup>[13]</sup> The ratio between these two compounds depends on the reaction temperature and the lower temperature favors the formation of **4** [4:5 = 80:20 (T = 80 °C) and 50:50 (T = 100 °C)]. The same result was obtained using in situ generated phosphaketene **3** from **2**. This synthetic method, avoiding the isolation of thermally labile **3**, is more convenient. Both products were successfully isolated by the precipitation of **5** as a yellow powder in pentane (Yield: 39%) and the following crystallization of **4** from the pentane solution at –30 °C (Yield: 31%). The presence of two phosphorus atoms in the cyclic phosphanylidene- $\sigma^4$ -phosphoranes **4** and **5** is clearly indicated by two AX-systems in the <sup>31</sup>P NMR spectrum (**4**:  $\delta = 88.5$  and 75.5 ppm,  $^1J_{\text{PP}} = 518.0$  Hz, **5**:  $\delta = -69.3$  ppm for  $\sigma^2$ -P and 69.8 ppm for  $\sigma^4$ -P,  $^1J_{\text{PP}} = 482$  Hz), and the large  $J_{\text{PP}}$ -coupling constants are in agreement with directly connected phosphorus atoms.<sup>[14]</sup> The <sup>31</sup>P NMR chemical shift of the phosphanylidene atom is generally observed at high field due to the strongly polarized ylidic  $\text{R}_3\text{P}^{\delta+} = \text{P}^{\delta-}\text{R}$  bond character,<sup>[15,16]</sup> which is the case for the carbonyl-substituted derivative **5**, exhibiting a signal  $\delta = -69.3$  ppm. In contrast, an unusual low-field chemical shift ( $\delta = 88.5$  ppm) is observed for the dicoordinate



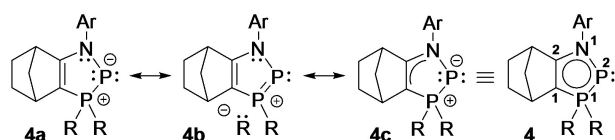
**Scheme 1.** Synthesis and thermolysis of plumbylene-substituted phosphaketene **3**.



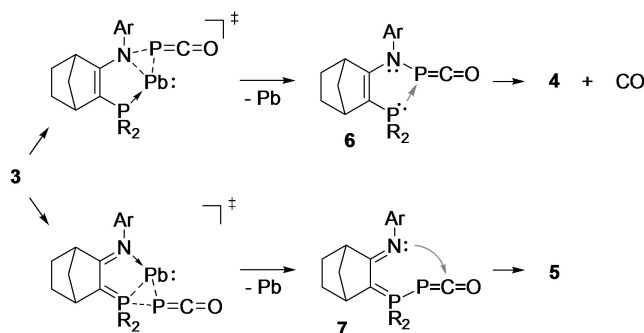
**Figure 2.** Molecular structures of **3** (left) and **4** (right). Thermal ellipsoids represent 30% probability. H and disordered atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: **3**: Pb–P2 2.761(5), P2–C3 1.591(8), C3–O 1.176(9), N1–Pb 2.315(2), Pb–P1 2.747(1), P1–C1 1.715(3), C1–C2 1.387(4), C2–N1 1.318(4), Pb–P2–C3 87.3(3), P2–C3–O 177.1(8), N1–Pb–P1 76.6(1), N1–Pb–P2 98.4(2), P2–Pb–P1 93.1(1), Pb–P1–C1 94.9(1), P1–C1–C2 122.5(2), C1–C2–N1 128.5(3), C2–N1–Pb 116.1(2). **4**: N1–P2 1.778(2), P2–P1 2.119(1), P1–C1 1.715(3), C1–C2 1.368(3), C2–N1 1.320(3), N1–P2–P1 92.1(1), P2–P1–C1 95.5(1), P1–C1–C2 114.7(2), C1–C2–N1 121.8(2), C2–N1–P2 115.9(1).

phosphorus atom of **4**, while the chemical shift for the four-coordinate P atom is similar to that observed for **5**. This suggests a cyclic  $\pi$ -delocalization of  $p_{\pi}$ -lone pair of electrons on phosphorus (Figure 3). Indeed, ligand-type dependence of  $^{31}\text{P}$  NMR chemical shifts of two-coordinate phosphorus atom in donor-stabilized phosphinidenes is well known and a low-field shift indicates a strong delocalization of phosphorus lone-pair towards the  $\pi$ -accepting ligand.<sup>[17]</sup> The similar low-field shift has been observed for the two-coordinate phosphorus atom in the 4-membered cyclic phosphanylidene phosphorane with a  $4\pi$ -electron system ( $\delta = 58$  ppm).<sup>[18]</sup>

The structure of **4** (Figure 2-right)<sup>[12]</sup> shows a N1-P2 atomic distance [1.778 Å] corresponding to a P–N single bond (ca 1.76 Å), and is significantly longer than N=P double bonds between tri-coordinated N and di-coordinated P atoms (1.61 Å). A similar N–P bond length (1.779 Å) was observed for the previously reported amine-substituted phosphorus two-coordinate anion.<sup>[19]</sup> The structure shows a shortening of the P1–C1 [1.715(3) Å] and C2–N1 [1.320(3) Å] bonds and a slight elongation of the C1–C2 bond [1.368(3) Å] compared to those in structure **5** (P1–C1: 1.741 Å, C2–N1: 1.376 Å, C1–C2: 1.360 Å). Furthermore, the P1–P2 bond length [2.119(8) Å] in **4**, which is similar to that observed for **5** [2.1006(7) Å], is intermediate between typical PP-single and -double bonds (2.22 Å and 2.04 Å).<sup>[20]</sup> These results suggest a cyclic  $\pi$ -electron delocalization, involving the tetracoordinated P1 atom through the  $\sigma_{\text{PN}}^*$  orbitals (**4b** in Figure 3). Similar cyclic delocalization phenomena have also been found for other  $\lambda^5$ -phosphorus containing cyclic molecules with  $6\pi$ -electrons.<sup>[21]</sup> The large low-field shift of the  $^{31}\text{P}$  NMR resonance observed for the P2 atom in **4** is also in good agreement with the cyclic  $\pi$ -electron delocalization (see Figure S3).



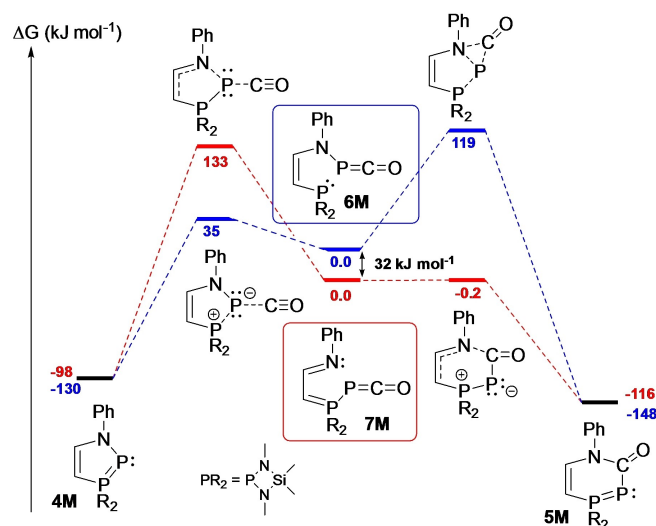
**Figure 3.** Some possible canonical structures of **4** involving the  $\text{PR}_2$  group via negative hyperconjugation.



**Figure 4.** Proposed mechanism for the thermal decomposition of the phosphino-stabilized plumbylene **3**.

Both compounds **4** and **5** are stable in solution, even at  $110^\circ\text{C}$ . Therefore, **5** is not the precursor of **4** via a CO elimination. Conversely, it was also confirmed that there was no reaction between **4** and CO (3 bar) even at  $110^\circ\text{C}$ . These results demonstrate that products **4** and **5** are obtained independently from  $\text{Pb}^{\text{II}}$ -substituted phosphaketene **3** via two different reaction pathways. Given the formation of metallic lead, probably **3** undergoes a reductive elimination at the  $\text{Pb}^{\text{II}}$  center in two different ways, generating two transient phosphaketene intermediates (**6** and **7**, Figure 4).

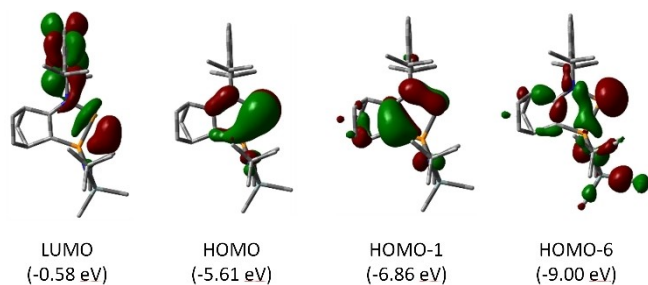
The reaction pathways for the formation of **4** and **5** were studied by DFT calculations at the M062X/6-311+G(d,p) level, using simplified model compounds **4M**–**7M** (Figure 5). The calculations show that (amino)phosphaketene **6M** is higher in energy than the isomeric (phosphanylidene)phosphaketene **7M** ( $\Delta G(398)_{7\text{M}/6\text{M}} = 32$  kJ mol $^{-1}$ ). This energy difference is only slightly larger (39 kJ mol $^{-1}$ ) for the actual molecules **6** and **7**. This small difference suggests that the model compounds are suitable for our purpose. The formation of both products, the amino-substituted phosphanylidene phosphorane **4M** and carbonyl-substituted one **5M** from **6M/7M** is exergonic and the latter is thermodynamically favored. The formation of **4M** from **6M** proceeds with a small barrier (35 kJ mol $^{-1}$ ) via substitution of the CO at the dicoordinate P atom by the phosphine. Likewise, the formation of **5M** from **7M** proceeds practically without a barrier via nucleophilic attack of the imine at the ketene carbon. Although we also found the pathways for the formation of **4M** and **5M** from **7M** and **6M** respectively, the calculated barriers for these transformations are considerably higher in energy (133 kJ mol $^{-1}$  and 119 kJ mol $^{-1}$ , respectively) and therefore they cannot compete the other pathways proceeding with much lower energy barriers. These results demonstrate that **4** and **5** are produced from the two specific intermediates (**6** and **7**) generated from the plumbylene **3** by two independent reaction pathways, by forming



**Figure 5.** Proposed mechanism for the transformation of phosphaketene intermediates **6M/7M** into **4M/5M**. Calculated relative Gibbs energies at 398 K in toluene,  $\Delta G(398)$  in kJ mol $^{-1}$  using M062X/6-311+G(d,p) relative to the energy of intermediates **6M** (in blue) and **7M** (in red).

either N–P or P–P bond by the reductive elimination of **3** at the Pb(II) center. Given the experimental results showing the slightly favored formation of **4** [4:5=80:20 (T=80 °C) and 50:50 (T=100 °C)], the production of intermediate **6** from the plumbylene **3** should be kinetically favored compared to that of intermediate **7** from **3**.

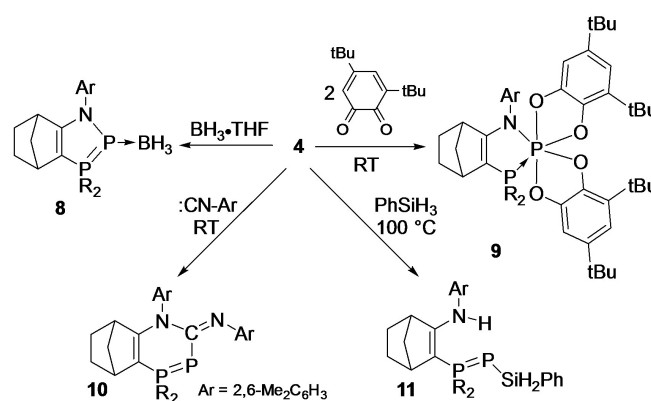
We investigated the electronic situation of **4** by the DFT calculations (M062X/6-311+G(d,p) level). The calculated pertinent structural parameters of **4** are very close to the values obtained by XRD analysis [no deviation in atomic distances larger than 3 %, see Supporting Information material (Table S1)]. The frontier orbitals HOMO and HOMO-1 of **4** are typical  $\pi$ -orbitals (Figure 6) and suggest delocalization across the five-membered P<sub>2</sub>NC<sub>2</sub>-ring (**4c** in Figure 3). An analysis based on natural bond orbital (NBO) theory indicates strong heteroallylic resonance across the C=C–N unit of the central five membered ring in addition to substantial delocalization from occupied  $\pi$ -type NBOs ( $\pi_{C1-C2}$ ,  $Lp_{P2}$ ) into  $\sigma^*_{P-N}$  NBOs on the tetra-coordinate P1 atom. (Figure S1). This interplay between  $\pi$ -resonance and negative hyperconjugation (cross-hyperconjugation) leads to an overall cyclic 6 $\pi$ -electron delocalization across the P<sub>2</sub>C<sub>2</sub>N-five membered ring (**4** in Figure 3) Indeed, the negative value of nucleus independent chemical shift (NICS) calculated for simplified model **4 M** (NICS(1): –6.9) suggests its aromatic character. This NICS(1) value is 70% of that predicted for the aromatic (C<sub>5</sub>H<sub>5</sub>)<sup>–</sup> and it is very similar to the values computed for the parent phosphole H<sub>2</sub>C<sub>4</sub>PH (NICS(1)=–6.2) and larger than predicted for the parent  $\lambda^5$ -phosphinine H<sub>5</sub>C<sub>5</sub>PH<sub>2</sub> (NICS(1)=–2.4, Figure S2).<sup>[22,23]</sup> Natural chemical shift (NCS) analysis reveals strong deshielding (paramagnetic) contributions from the  $\pi$ -type lone pair at P2.<sup>[24]</sup> This deshielding is a result of an interaction between the orthogonal  $\pi$ -type lone pair and the  $\sigma^*_{P2-N1}$  orbitals at P2 induced by the external magnetic field (Figure S3).<sup>[25]</sup> The HOMO of **4** is a  $\pi$ -type orbital with dominant contributions from the P2 atom (**4a** in Figure 3). The LUMO has antibonding character between the P1 and N1 atoms ( $\sigma^*_{PN}$ ) which is orthogonal relative to the HOMO. Notably, this sequence and spatial orientation of the frontier orbitals is inverse to regular carbene analogues (in plane-HOMO,  $\pi$ -type LUMO). In line with these orbital considerations is the relative large electron accumulation at the P2 atom computed in **4** (Natural charge: +0.02 a.u. at P2 vs. +1.58 a.u. at P1) and a strong negative electrostatic potential at this atom (Figure S4).



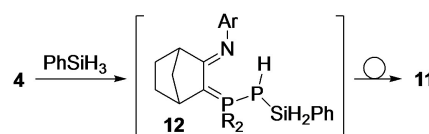
**Figure 6.** Calculated frontier molecular orbitals of **4** and their energies at the M06-2X/6-311G(d,p)//M06-2X/6-311+G(d,p) level (isosurface level =  $\pm 0.04$  e/(a.u.)<sup>3</sup>). Hydrogen atoms were omitted for the clarity.

As indicated by the MO analysis, compound **4** shows large electron density localization at the two-coordinate P2 atom, which results in considerable electron repulsion with the adjacent N atom to weaken the P2–N bond (**4a** in Figure 3). Therefore, **4** presents a nucleophilic character at the dicoordinated P2 atom and the cleavage of the P2–N bond is preferred. Indeed, **4** cleanly reacts with BH<sub>3</sub>·THF at the P2 atom to give the corresponding donor-acceptor complex **8** (Scheme 2).<sup>[26]</sup> As expected, **4** reacts readily with two equivalents of 3,5-di-tert-butyl-benzoquinone at the phosphorus atom to form the corresponding hexa-coordinated phosphorus product **9**. The same reaction has already been described with the previously reported cyclic and acyclic phosphanylidene-phosphoranes.<sup>[27,28]</sup> The labile nature of the P–N bond was demonstrated by the reaction of **4** with the amphiphilic 1,3-dimethylbenzo isonitrile leading to an isonitrile insertion reaction to give the corresponding cyclic phosphanylidene-phosphorane **10** in contrary to the reaction of acyclic Ar–P=PMe<sub>3</sub> with an isonitrile leading the replacement of phosphine ligand to afford the corresponding 1,3-phosphaazoallene.<sup>[29]</sup> In addition, **4** also undergoes a 1,2-addition of phenylsilane to the P–N moiety cleaving the P–N bond (formal metathesis of the Si–H/P–N bond) to give a new P-silylated phosphanylidene-phosphorane **11**.

Given the polarity of the Si( $\delta^+$ )–H( $\delta^-$ ) and N( $\delta^-$ )–P( $\delta^+$ ) bonds, the direct formation of **11** by the 1,2-addition of PhSiH<sub>3</sub> to the P–N moiety of **4** is unlikely. Instead, the reaction probably starts with the 1,1-addition (oxidative addition) of phenylsilane to the two-coordinate phosphorus atom of **4** to generate the corresponding phosphine derivative **12** (Figure 7). Subsequent isomerization of **12** by intramolecular deprotonation of the P–H group by the conjugated phosphazene moiety yields **11**.



**Scheme 2.** Reactions of phosphanylidene- $\sigma^4$ -phosphorane **4**.



**Figure 7.** Proposed mechanism for the reaction of **4** with PhSiH<sub>3</sub>.



## Conclusion

In conclusion, we synthesized a new stable plumbylene-substituted phosphaketene **3** by the successive reactions of  $\text{PbCl}_2$  with two anionic reagents (amidophosphine **1** and  $\text{NaPCO}$  salt). This phosphaketene **3** evolves under mild conditions, by reductive elimination at the  $\text{Pb}^{\text{II}}$  center forming new N–P and P–P bond, to generate the transient amino- and phosphanylidene-phosphaketenes **6** and **7**. Of particular interest, the (amino)phosphaketene **6** evolves further to a new heterocyclic (amino)phosphanylidene phosphorane **4**, which shows a unique phosphinidenoid reactivity.<sup>[30]</sup> This new alternative route for the generation of phosphaketenes, compared to the classical route, should extend and facilitate further their access. Applications of this new methodology to obtain other phosphaketenes and phosphinidenes, which are difficult to access by conventional methods, are under active investigation.

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## Conflict of Interest

The authors declare no conflict of interest.

## Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

**Keywords:** heterocycles · phosphaketenes · phosphanylidene · phosphinidenes phosphoranes · plumbylene

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