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# Theoretical and structural studies on mechanism of the Stec reaction

Maria del Carmen Michelini<sup>b</sup>, Nino Russo<sup>b</sup>, Stefano Alcaro<sup>c</sup>, Lucyna A. Wozniak<sup>a,d,\*</sup>

<sup>a</sup> Medical University of Lodz, Department of Structural Biology, 90-752-Lodz, 7/9 Zeligowskiego Str., Poland

<sup>b</sup> Department of Chemistry, University of Calabria, Arcavacata di Rende, Italy

<sup>c</sup> Dipartimento di Scienze Farmacobiologiche Università di Catanzaro "Magna Grécia", Complesso Ninò Barbieri, 88021 Roccelletta di Borgia (CZ), Italy

<sup>d</sup> Centre of Molecular and Macromolecular Studies, Department of Bioorganic Chemistry, Polish Academy of Sciences, Lodz, Poland

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## ABSTRACT

The mechanism of the Stec reaction between phosphoroselenanilidate or phosphonoanilidate and CS<sub>2</sub>, activated by strong bases, has been studied computationally, using DFT methods, and experimentally, by low temperature <sup>31</sup>P NMR spectroscopy. From molecular calculations, the reaction pathway of the reaction has been revealed with several transition states and intermediates, including a low energy spirocyclic pentacoordinate transition state and acyclic tetracoordinate intermediates, which eventually were correlated with short living molecules detected by NMR spectroscopy.

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# 1. Introduction

The Stec reaction, namely the  $PN \rightarrow PX$  (X=O, S, Se) conversion, has been established as a convenient method for the synthesis of numerous P-chiral phosphates, and their thio- or seleno-congeners, which otherwise could not be simply prepared. Since the reaction is stereospecific, the P-chiral phosphoramidates are valuable precursors for the synthesis of a variety of P-chiral derivatives of phosphorus acids, including various biophosphates and their analogues.<sup>1</sup> More recently, the  $PN \rightarrow PX$  reaction was applied in a stereoconvergent synthesis of stereodefined methylphosphonate analogues of nucleic acids with a predetermined sense of chirality at the internucleotide methylphosphonates.<sup>2</sup>

The exhaustive studies<sup>3</sup> confirmed a stereoretentive pathway<sup>4</sup> for this reaction for acyclic and cyclic (five- or six-membered ring) compounds alike. It was postulated that the reaction occurred by the attack of the phosphylamidate anion **II** at the carbonyl atom of chalcogenide (Scheme 1),<sup>5</sup> with formation of the adduct **III**. It was assumed that the adduct **III** could intramolecularly rearrange, forming putative pentacoordinate intermediate **IV**. Such intermediate should undergo a polytopal rearrangement into another pentacoordinate intermediate **V**. The Westheimer's rules of apical entry—apical departure, required placing the nitrogen atom into an apical position, necessary for the P–N bond cleavage.<sup>6</sup> A participation of hypervalent intermediates of square/rectangular structure **VI** stayed questionable. The odd number of polytopal rearrangements (either Berry pseudorotation Y, or turnstile

rotation TR) within the pentacoordinate intermediate(s) would result in retention of configuration at the phosphorus atom. The synchronous cleavage of the P–N and C–Y bonds also lead to the corresponding phosphates (or their analogues) with the retained configuration at phosphorus, and the nitrogen cumulene-like RN= C=X as a second product.

It should be underlined that although the mechanism presented in Scheme 1 supports the stereoretentive mode of the  $PN \rightarrow PX$ conversion, the experimental evidence for the putative participation of intermediates of either structure **III** or **VI** was lacking.

For clarifying the mechanism we merged Density Functional Theory (DFT) studies of the potential energy profiles, supported with the structural parameters obtained from the X-ray data and the low temperature NMR experiments, focused on detection and identification of any 'short-time living' species.

As model compounds, the selenium analogue of pyrocatechol, i.e., 2-*N*-phenylamine-2-seleno-1,3,2-benzodioxaphospholane (1) (Scheme 2) was chosen since there are existing stable  $P^V$  phosphoranes with the 1,2-benzenediol group located in the apical–equatorial position, which hinders molecules in predictable conformations.<sup>7</sup>

# 2. Results and discussion

## 2.1. Synthesis and reactivity

2-Aniline-2-seleno-1,3,2-benzodioxaphospholane (**1**) was prepared from 2-chloro-1,3,2-benzodioxaphospholane (**2**), treated with an excess of aniline (2 equiv) at room temperature in toluene in the presence of elemental selenium. The conversion to the initial  $P^{III}$  derivative, i.e., 2-aniline-1,3,2-benzodioxaphospholane (**3**) (<sup>31</sup>P



<sup>\*</sup> Corresponding author. Tel.: +48426393221; e-mail addresses: lucyna.wozniak@umed.lodz.pl, lawozniak@gmail.com (LA. Wozniak).

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Scheme 1. Plausible mechanism of the  $PN \rightarrow PS$  reaction between 2-*N*-phenylamine-2-seleno-1,3,2-benzodioxaphospholane 1 (activated with strong bases) and carbon disulfide.<sup>13</sup>



Scheme 2. Synthesis of 2-aniline-2-seleno-1,3,2-benzodioxaphospholane (1) and  $^{31}P$  NMR chemical shifts and coupling constants  $^{1}J_{P-Se}$ .

NMR  $\delta$  137.22 ppm) was complete within 15 min at room temperature. The addition of selenium required phosphoramidite **3** to be heated in a sealed ampoule for several days in toluene, producing **1** in good yields (over 90% as estimated from <sup>31</sup>P NMR spectroscopy). In contrast, it is worth emphasizing, that addition of elemental sulfur to **3** providing the corresponding 2-aniline-2-thio-1,3,2benzodioxaphospholane (**4**) was formed at room temperature within 4 h in almost quantitative yield, and **4** was easily purified by a silica gel column chromatography.

Our efforts to separate the phosphoroselenoanilidate **1** by column chromatography under analogous conditions failed. Instead, the 2-oxo-2-seleno-1,3,2-benzodioxaphospholane (**5**) (<sup>31</sup>P NMR  $\delta$  65.2 ppm, <sup>1</sup>*J*<sub>PSe</sub>=915 Hz) was collected from the column as the major product accompanied by traces of *N*-phenyl-*N*,*N*-bis(2-seleno-1,3,2-benzodioxaphospholane) (**6**) (<sup>31</sup>P NMR  $\delta$  73.2 ppm, <sup>1</sup>*J*<sub>PSe</sub>=1005 Hz) with no trace of **1** collected after chromatography (Scheme 3).

The structure of **5** was confirmed by the X-ray analysis.<sup>8</sup> Additionally, it was established that 2-oxo-2-seleno-1,3,2-benzodioxaphospholane (**5**) was easily oxidized under mild anhydrous conditions with *t*-BOOH, yielding in 1,3,2-benzodioxaphospholane (**7**) (<sup>31</sup>P NMR  $\delta$  – 1.8 ppm). Compound **5** after treatment with bis(-trimethylsilyl)acetamide provided exclusively 2-trimethylsilyloxy-2-seleno-1,3,2-benzodioxaphospholane (**8**) (<sup>31</sup>P NMR  $\delta$  63.1 ppm,  $^{1}J_{P-Se}$ =1061 Hz). Reaction of **5** with Mel led to 2-methoxy-2-seleno-1,3,2-benzodioxaphospholane (**9**) ( $^{31}$ P NMR  $\delta$  65.9 ppm,  $^{1}J_{P-Se}$ =1041 Hz).

The progress of the  $PN \rightarrow PS$  reaction was followed by <sup>31</sup>P NMR spectroscopy. It was found that the activation of **1** with strong bases resulted in stable anionic forms **11**, in the presence of NaH ( $\delta$  56.1 ppm, <sup>1</sup>J<sub>P-Se</sub>=885 Hz ), and DBU ( $\delta$  57.3 ppm, <sup>1</sup>J<sub>P-Se</sub>=910 Hz), respectively. The reaction of the anionic 2-aniline-2-seleno-1,3,2-benzodioxaphospholane (**11**) with an excess of CS<sub>2</sub> performed either in MeCN, THF, or DMF resulted in formation of the expected 2-thio-2-seleno-1,3,2-benzodioxaphospholane (**12**) in almost quantitative yields (Scheme 4).

### 2.2. Theoretical studies

The Stec reaction, being a variant of the Horner– Wadsworth–Emmons (HWE) reaction of dialkyl (aryl) phosphoramidates (usually anilidates), activated by sodium hydride, with carbonyl electrophiles or carbon disulfide to provide dialkyl phosphates and the corresponding isocyanates or isothiocyanates, was extended to phosphoramidothioates ( $\mathbf{2}, X=S$ ) and phosphoramidoselenoates ( $\mathbf{2}, X=Se$ ) with the purpose obtaining several phosphorus acid derivatives, particularly P-chiral compounds in stereospecific manner.<sup>1–4</sup> Therefore, the question of the mechanism of stereospecific



**Scheme 3.** Reactivity of **1** ( ${}^{31}$ P NMR chemical shifts and coupling constants  ${}^{1}J_{P-Se}$ ).



Scheme 4. Synthesis of 2-thio-2-seleno-1,3,2-benzodioxaphospholane (12).

formation of these products has been of special interest. Here we report a theoretical approach to the reactions of 2-*N*-phenylamine-2-seleno-1,3,2-benzodioxaphospholane (**3**) and 2-*N*-phenylamine-2-oxo-1,3,2-benzodioxaphospholane (**7**) with CS<sub>2</sub>, with special emphasis on the structures of  $P^V$ -intermediary structures.

Numerous computational investigations have been reported using quantum mechanical calculations to elucidate the HWE and related reactions, mostly focused on the stereochemistry of alkene formation.<sup>9</sup> From these studies it was clear that these reactions can be rationalized by including solvation effects, since previous calculations on mechanism and stereoselectivity of ylide reactions carried out as the gas-phase potential energy surface were not evocative.<sup>10</sup> Brandt et al. investigated the HWE reaction using highlevel quantum chemical (QC) methods. They found that the model reaction of trimethyl phosphonoacetate and formaldehyde was very sensitive to solvent effect and the rate limiting step was connected to a formation of the oxyanion corresponding to structure III (Scheme 1).<sup>11</sup>

The initial step was to model the gas-phase reactions. With this aim, theoretical calculations of all the reactants, intermediates, transition states, and products were performed within the framework of DFT. In particular, the Perdew and Wang density gradient correction to the exchange and correlation functionals (denoted as PW91PW91) was used,<sup>12–14</sup> together with the aug-cc-pVTZ-PP basis set for selenium,<sup>15</sup> and 6-311++G(2d,2p) extended basis set<sup>16–18</sup> for the rest of the atoms. All the calculations were carried out with Gaussian03 code.<sup>19</sup> We refer to this level of calculation as PW91/G03, hereafter.

All geometrical structures were optimized without symmetry restrictions. For each optimized system a vibrational analysis was performed to determine its character (minima or saddle point) and to evaluate the zero-point vibrational energy corrections (ZPVE), which were included in all the reported energies. We have ensured that every transition state has only one imaginary frequency, and that the vibrational mode associated to that frequency corresponds to the correct movement of the involved atoms. All the minima connected by a given transition state were confirmed performing IRC (Intrinsic Reaction Coordinate) computations, as implemented in Gaussian03 program.<sup>20</sup> The default SCF=tight keyword was used in all geometry optimizations. However, in order to check for the

reliability of some of the transition states that show low imaginary frequencies (less than  $100 \text{ cm}^{-1}$ ), we have re-optimized those structures using the SCF=very tight option of Gaussian03. No changes were found in the optimized geometries or the imaginary frequencies of those structures.

For both studied reactions, we report the gas-phase Potential Energy Profiles (PEPs) calculated as relative energies (including ZPVE) of the species involved in the reaction pathways with respect to the ground-state reactant asymptotes at 0 K.

Single point calculations were performed on the gas-phase optimized structures in order to include solvent effects. Those effects were computed within the framework of the Self-Consistent Reaction Field Polarized Continuum Model (SCRF-PCM)<sup>21–23</sup> as implemented in Gaussian03. The default UAHF33 set of solvation radii was used in the calculations to build the cavity according to the molecular topology, hybridization, and formal charge. In this method, the solvent is modeled as a continuum of dielectric constant  $\varepsilon$ . In order to determine the solvent effects on the reaction energetic, each of the species along the reaction pathways is placed in a cavity within the solvent. The polarized continuum model defines the cavity as the union of a series of interacting spheres centered on the atoms, and uses a numerical representation of the polarization of the solvent. This type of model, however, does not consider specific interactions between the solute and the solvent.

After inclusion of solvent effects on each of the species involved in the reaction mechanism, the PEPs are reconstructed as relative energies (including the gas-phase ZPVE correction) with respect to the corresponding reactant asymptotes.

We first analyzed the gas-phase PEPs of reactions  $PN(Se) \rightarrow P(S)$ Se and  $PN(O) \rightarrow P(S)O$  (Fig. 1) The geometrical structures of the all the involved stationary points are reported in Figs. 2 and 3, respectively.

The reaction of the phosphoroselenoanilidate anion **11** (R1) and  $CS_2$  starts with the surpassing of an activation barrier of about 11 kcal/mol (**TS1**). It is important to indicate that in the first transition state (**TS1** *i*252 cm<sup>-1</sup>, Fig. 2) the  $CS_2$  molecule is already activated, as evidenced by the S(1)–C(3)–S(2) angle of 142.8°. After the system surpasses the first transition state, the formation of the first insertion intermediate (**Int1**), takes place. In this structure the C–N bond can be considered as already formed (1.478 Å). Further



**Fig. 1.** Gas-phase potential energy profiles for reaction  $PN(Se) \rightarrow P(S)Se$  (full line) and  $PN(O) \rightarrow P(S)O$  (dashed line). The relative energies (RE, in kcal/mol) of the transition states, intermediates and products are calculated with respect to the ground-state reactant asymptotes (R1+CS<sub>2</sub> and R1'+CS<sub>2</sub>, respectively).

diminishing of the S(1)-C(3)-S(2) angle  $(127.1^{\circ})$  and a slight lengthening of the C-S bonds are also evidenced in this structure (Fig. 2). The formation of this intermediate is endothermic by 8 kcal/ mol. The system then overcomes the second transition state (TS2.  $i126 \text{ cm}^{-1}$ ), which involves a reaction barrier of 4 kcal/mol. **TS2** is 12 kcal/mol above the reactant asymptotes and is structurally very close to **TS1**, with the major shortening of the P-S(1) distance, from 3.245 Å in the first intermediate to 2.855 Å in the TS2. The reaction then proceeds to the formation of a second insertion intermediate (Int2) with a four-member ring hypervalent pentacoordinate spirocyclic structure. Int2 is more stable than Int1 by around 17 kcal/ mol and is 9 kcal/mol below the reactants asymptote. The last step of the reaction takes place after the system surpasses the last transition state (**TS3**, *i*78 cm $^{-1}$ ), which involves a reaction barrier of 7 kcal/mol. This step is associated with the cleavage of N–P and C(3)-S(1)bonds. Our calculations indicate that the overall process, from reactants to products, is exothermic by 11 kcal/mol.

A similar reaction mechanism can be traced for  $PN(O) \rightarrow P(S)O$ . The potential energy profile for the gas-phase reaction is sketched in Fig. 1 (dashed line), with the optimized geometries of all the involved species reported in Fig. 3.

The initial barrier height is only slightly lower than that for  $PN(Se) \rightarrow P(S)Se$ , namely 9 kcal/mol over the asymptote limit. The first insertion intermediate (Int1') is more stable than the corresponding minima for the previous reaction by around 5 kcal/mol. The next step of the reaction involves the overcoming of the second transition state (TS2'), which involves an energetic barrier of 5 kcal/mol. TS2' is 8 kcal/mol above the reactant asymptotes, and is characterized by an imaginary frequency  $(i124 \text{ cm}^{-1})$  that involves the stretching of the P-S(2) bond (Fig. 3).<sup>12</sup> As compared to the previously described reaction, the geometrical structure of TS2' is very close to that of (I'), albeit the major difference between the structures is reflected in the P-S(2) distance. After the system surpasses the second transition state, the formation of a second insertion intermediate (Int2') takes place. The implied exothermic effect is of about 15 kcal/mol. As in the previous reaction, Int2' is more stable than the previous reaction intermediate, by around 9 kcal/mol. In contrast to the reaction  $PN(Se) \rightarrow P(S)Se$ , the reaction  $PN(O) \rightarrow P(S)O$  products are slightly higher in energy with respect to the last intermediate. The whole reaction was found to be exothermic by around 11 kcal/mol.

As previously mentioned, the solvent effects were evaluated by performing single point calculations on the gas-phase optimized geometries, using the SCRF-PCM approach. We have considered two different solvents, namely MeCN and THF. The computed potential energy profiles for the  $PN(Se) \rightarrow P(S)Se$  reaction including solvent effects are reported in Fig. 4 and compared with gas-phase PEP. The inclusion of the solvent effects induces important changes in the shape of the PES. Indeed, the initial barrier increases by around 3 kcal/mol with respect to the gas-phase value. In contrast, the insertion intermediate (**Int1**) and the second transition state (**TS2**) show higher stabilities. The second insertion intermediate (**Int2**) and the last transition state (**TS3**) are destabilized by 3 and 4 kcal/mol, respectively. The exothermic effect of the whole process is increased with respect to the gas-phase value by around 5 kcal/mol.

The gas-phase PEPs for the  $PN(O) \rightarrow P(S)O$  reaction are changed by the inclusion of solvent effects in a similar way. In particular, there is an increase in the first barrier of around 5 kcal/mol, whereas the first insertion intermediate (**Int1**') and the second transition state (**TS2**') are more stabilized than in the gas-phase reaction by 4 and 2 kcal/mol, respectively. The second insertion intermediate (**Int2**') is slightly less stabilized, with respect to the asymptotes than in the gas-phase reaction, being at 7 kcal/mol under the reactant asymptote. The same effect is found for the last transition state, **TS3**', by about 4 kcal/mol. From reactants to products, the process is exothermic by around 16 kcal/mol (Fig. 5).

# 2.3. <sup>31</sup>P NMR studies

It was found that the activation of phosphoramidates can be efficient not only in the case of sodium or potassium hydrides, but also can be achieved in the reactions of strong organic bases. Among them DBU was found to be superior because of solubility and homogeneity of the reaction system. From previous experiments it is known, however, that DBU activation results in slower conversion, therefore low temperature reactions were performed in DMF and THF, with NaH as activator.

It was found that at  $-60 \degree C$  the activation in DMF was almost simultaneous, and two closely resonating compounds were formed (<sup>31</sup>P NMR  $\delta$  57.75 ppm, <sup>1</sup>*J*<sub>PSe</sub>=890 Hz; 58.66 ppm, <sup>1</sup>*J*<sub>PSe</sub>=906 Hz) in a 2:1 ratio. The signal of the higher field species disappeared first (at  $-40 \degree C$ ), whereas the second one disappeared slowly in the course of the reaction and corresponded to formation of 2-thio-2-seleno-1,3,2-benzodioxaphospholane (**12**) (<sup>31</sup>P NMR  $\delta$  120.66 ppm, <sup>1</sup>*J*<sub>PSe</sub>=876 Hz). The initial 2:1 ratio of the preliminary intermediate species is invariable in different solvents like THF (at  $-40 \degree C$ ) or at MeCN (at  $0 \degree C$ ), and product **12** formation is always accompanied by the disappearance of the corresponding intermediate at  $\delta$  57.75 ppm, <sup>1</sup>*J*<sub>PSe</sub>=890 Hz.

At –25 ppm and –40 ppm, we observed traces of relatively long living species (below 10%). Their chemical shifts imply pentacoordinate phosphorus compounds.<sup>7b,24</sup> However, based on the chemical shifts it is unfeasible to assess their structure, since there are limited data on pirocatechol phosphoranes,<sup>25</sup> particularly those with spiro structures involved.<sup>26</sup> We have not detected any <sup>1</sup>*J*<sub>P-Se</sub> coupling constants, therefore the presence of selenium in high field compounds cannot be confirmed. There are literature reports, however, of several selenium containing P<sup>V</sup> compounds lacking a <sup>1</sup>*J*<sub>P-Se</sub>, although a reason for this phenomenon is not clear.<sup>27</sup>

<sup>31</sup>P NMR chemical shifts were calculated using the Gauge Invariant Atomic Orbital Method (GIAO)<sup>28</sup> with both Gaussian03 and ADF2004.01 packages.<sup>29</sup> In the case of Gaussian03 calculations, we employed the mPW1PW91<sup>30</sup> functional on the PW91PW91/cc-augpVTZ-PP(Se), 6-311G++(2d,2p) optimized geometries, using the same basis sets (mPW1PW91/G03, hereafter).

Previous theoretical studies have also shown the difficulty in suggesting a reliable choice of a functional, due to the significant variance in performance of the different methods,<sup>31</sup> with the mPW1PW91 functional found to have a good performance in previous NMR chemical shift theoretical studies.<sup>31a</sup> We also performed



**Fig. 2.** Most relevant geometrical parameters of the species involved in the  $PN(Se) \rightarrow P(S)Se$  reaction. Bond distances are in angstroms and angles in degrees. Imaginary frequencies are reported between parentheses.

some test calculations using the B3LYP functional,<sup>32</sup> which has also been reported to be efficient for the calculation of NMR properties.<sup>33</sup> However, for the systems under study it was found that the mPW1PW91 functional gave a better agreement with the observed values. We therefore report the results obtained at the mPW1PW91/cc-aug-pVTZ-PP(Se), 6-311G++(2d,2p) level of theory (mPW1PW91/G03).

The NMR spin—spin coupling constants were calculated using the ADF package. The zero-order regular approximation (ZORA) was employed in all ADF calculations. For these calculations we chose the PW91 functionals (exchange and correlation) together with the TZ2P basis sets, as implemented in ADF code (PW91/ADF, hereafter). All ADF calculations were performed after the structures were re-optimized at the same level of theory used for NMR calculations. The geometrical parameters obtained at the PW91/ADF level of theory with the ADF program for substrate **1**, and its anion **11**, **Int1**, **Int2** and the product P1 are presented at Fig. 6, together with the corresponding values obtained at the PW91/G03 level. A comparison between the structural parameters obtained at the different levels of theory shows that there is a fairly good agreement, in particular the bond distances differ by less than 0.02 Å and angles by less than 6°. The difference between calculated dihedral angles was in some cases a little larger, namely up to 15° (substrate **1**). The computed <sup>31</sup>P chemical shifts are reported in Table 1 together with the measured values, whereas the different contributions to the spin–spin coupling constants are given in Table 2.



Fig. 3. Most relevant geometrical parameters of the species involved in the  $PN(O) \rightarrow P(S)O$  reaction. Bond distances are in angstroms and angles in degrees. Imaginary frequencies are reported between parentheses.

A comparison between the <sup>31</sup>P chemical shifts computed for substrate **1** and the anionic structures **R1** and **12** (**P1**); and the corresponding measured values shows that even when the trend is well reproduced, the differences between the measured chemical shifts and the calculated ones are significant. As previously demonstrated, theoretical modeling of phosphorus NMR chemical shielding is very challenging.<sup>34</sup> The chemical shifts are known to be very sensitive to the molecular geometry.<sup>34b,35</sup> Accordingly, one of the reasons for the quantitative disagreement observed between the calculated and experimental values could be the approach used for the inclusion of solvent effects. Due to the excessive computational cost of performing geometry optimizations including solvent effects, single point calculations were done on gas-phase optimized geometries. A comparison between the computed values shows that, in all cases the calculations overestimate the experimental values, and that the inclusion of the solvent effects does not notably improve the agreement. With the only exception of substrate **1**, all of the species studied here are negatively charged and both media (MeCN and THF) are relatively polar, therefore solvent effects are expected to be strong. Between the theoretical approaches used here, the one that gives the better agreement with the experiments is PW91/ADF, which could be due to the better performance of the TZVP Slater-type basis sets. However, we have not performed a complete comparison of different functional/basis sets as to conclude that the better performance is mainly associated to the functional or basis sets employed in each approach.



**Fig. 4.** Potential energy profile for  $PN(Se) \rightarrow P(S)Se$  reaction including solvent effects for MeCN (full line) and THF (dashed line). The gas-phase PEP is included as a reference (dotted line).



**Fig. 5.** Potential energy profile for the  $PN(O) \rightarrow P(S)O$  reaction including solvent effects for MeCN (full line) and THF (dashed line). The gas-phase PEP is included as a reference (dotted line).

We have obtained better results for the calculated values of coupling constants at the PW91/ADF level of theory, for 2-aniline-2seleno-1,3,2-benzodioxaphospholane (1) ( $J_{P-Se}$ =1040 Hz) where they almost merge with the experimental ones ( $J_{P-Se}$ =1018 -1028 Hz), and, with a slightly less accurate value for the anionic species **11**.

# 3. Conclusions

Over the past few decades quantum mechanical calculations have provided considerable insight into the mechanisms of chemical reactions. Careful examination of the potential energy profiles calculated by QM/MM methods, support or question a mechanism due to possibility of evaluation of structures proposed for presumed transition states and intermediates.<sup>10,11</sup>

It is accepted that the Stec reaction, being a particular variation of the Wordsworth–Emmons reaction (Scheme 1), involves a two-step process: an initial addition of an electrophile to the activated phosphoramidates (or their thio- or seleno-analogues), followed by formation of intermediates (and their rearrangements), with simultaneous break of the P–N and C–S bonds and elimination of cumulene, resulting in formation of the corresponding phosphate, phosphorothioate, or phosphoroselenoate, respectively. Pentacoordinate intermediates with a four-membered ring have been postulated and their intermolecular rearrangements according to the Westheimer rules have been assumed to be responsible for the stereoretentive mechanism of this reaction.<sup>1,3</sup> However, so far, experimental evidence of these hypervalent species has not been available.

In practice, the definite pentacoordinate structures could vary between the TBP (like structures **IV** and **V** in Scheme 1) and the square/rectangular pyramidal (SP/RP) (structure **VI**) geometry. In general, the TBP geometry, with a different level of distortion, is favored, and the SP/RP geometry is mostly limited to spirobicyclic derivatives or ones containing strained three-/four-membered rings.<sup>36</sup> It is experiential that a less apicophilic thio or seleno group in the TBP geometry is more apicophilic in the SP/RP geometry.<sup>37</sup>

Intramolecular exchange processes in acyclic pentacoordinate phosphoranes appear to occur mostly through a Berry pseudorotation.<sup>38</sup> Even for a monocyclic and spirocyclic phosphorane, this is a good option, although in principle a turnstile mechanism could also be operating. Barriers of pseudorotation are influenced by charge state, apicophilicity of ligands, intramolecular hydrogen bonding, cyclic structure, and solvation.<sup>39</sup>

In the case of the reaction of anion **11** with CS<sub>2</sub>, the initial addition resulted in transition state TS1 (the energy barrier was calculated as 11 kcal/mol in the gas phase, and corrected to 14 kcal/mol in MeCN). The first minimum in the potential energy surface (**Int1**) corresponding to the intermediate of tetracoordinate structure **III** was identified with 8 kcal/mol in the gas phase dropping to 5 kcal/mol in MeCN. One can take into consideration the relatively small differences in structure between **II** and **III** (R1 and **Int1** in Fig. 3), and compare it with variable temperature NMR data, where the signal of anion **11** is accompanied at low temperatures by a close but distinguishable higher field signal (<sup>31</sup>P NMR  $\delta$  57.75 ppm, <sup>1</sup>*J*<sub>P-Se</sub>=890 Hz and 58.66 ppm <sup>1</sup>*J*<sub>P-Se</sub>=906 Hz), originally in a 2:1 ratio. If so, one could assume this signal of being a tetracoordinate ionic intermediate **III** (Int1, <sup>31</sup>P NMR  $\delta$  57.75 ppm, <sup>1</sup>*J*<sub>P-Se</sub>=890 Hz).

The second minimum of the potential energy profile corresponds to a spirocyclic pentacoordinate intermediate of the postulated structure **V** (**Int2** in Fig. 2). The formation of this intermediate is preceded by an overcoming of the second energy barrier lowered in solvent to 10 kcal/mol and transition state **TS2**.

The second intermediate, which is a priori more stable (structure **V**), and should be a result of pseudorotation<sup>40</sup> with the P–S bond placed in an apical position, has a distorted structure of TBP with SePO(1) and SePO(2) angles of 99.1° and 121.1°, respectively. The structure of the second intermediate of the  $PN(O) \rightarrow P(S)O$  reaction shows very similar characteristics, with the representative angles O(3)PO(1)=118.2° and O(3)PO(2)=100.3°, respectively. In both intermediates, the PO(1) and PO(2) distances are not equal,<sup>11</sup> additionally confirming the distorted structures of these species. On the potential surface there is no identified structure of preliminary pentacoordinate species IV, which would evolve via pseudorotation to V. Such a result, however, is not completely unexpected. Recently, the ab initio studies at RHF and B3LYP levels of theory of the Staudinger reaction showed that the mechanism would produce a pentacoordinate intermediate with a four-membered ring with the sp<sup>3</sup> nitrogen atom in an apical position.<sup>41</sup> However, the cyclization transition state (analogous to intermediate III of the Stec reaction) was found to convert directly into more a stable isomer without intermediacy of the initial pentacoordinate.

The question arises about the rate limiting step, and relevance of assignment of the <sup>31</sup>P NMR signal close to the anion **11** as an intermediate. Since the inclusion of the solvent effect increases the initial barrier by around 3 kcal/mol with respect to the gas-phase, the intermediate and the second transition state (**TS2**) show



Structure of substrate 1

| DSa: 2 061(2 059)        | O(1)C(1), 1 284 (1 282)        |
|--------------------------|--------------------------------|
| PSe. 2.001(2.038)        | O(1)C(1). 1.384 (1.382)        |
| PN: 1.666(1.673)         | O(2)C(2): 1.387 (1.389)        |
| PO(1): 1.686(1.676)      | NC <sub>4</sub> : 1.428(1.414) |
| PO(2): 1.677 (1.673)     |                                |
| NPSe: 118.2 (118.6)      | O(1)PN: 105.6 (107.2)          |
| SePO(1): 116.4 (113.9)   | O(2)PN: 99.9 (97.8)            |
| SePO(2): 118.7 (120.9)   |                                |
| dihedral angle: C(1)C(2) | C(4)C(5): -46.5 (-30.5)        |
|                          |                                |



Int1

PSe: 2.093 (2.090)

PN: 1.687 (1.685)

PO(1): 1.680 (1.677) PO(2): 1.680 (1.677) NPSe: 115.3 (115.4)

SePO(1): 112.5 (112.4)

SePO(2): 112.5 (112.5)

2 (118.6) O(1)PN: 105.6 (107.2) 16.4 (113.9) O(2)PN: 99.9 (97.8) 18.7 (120.9) gle: C(1)C(2)C(4)C(5): -46.5 (-30.5) S(1) = C(3) = C(5)S(1) = C(5) = C(5)

O(1)C(1): 1.375 (1.374)

O<sub>2</sub>C<sub>2</sub>: 1.375 (1.374)

 $NC_3$ : 1.474 (1.476)  $NC_4$ : 1.451 (1.451)

O1PN: 109.9 (110.0)

O<sub>2</sub>PN: 109.9 (109.9)



 $\begin{array}{c|c} Structure \ of \ anionic \ 11\\ PSe: \ 2.121 \ (2.112) & O(1)C(1): \ 1.358 \ (1.356)\\ PN: \ 1.361 \ (1.571) & O(2)C(2): \ 1.361 \ (1.361)\\ PO(1): \ 1.741 \ (1.700) & NC(4): \ 1.376 \ (1.373)\\ PO(2): \ 1.718 \ (1.702) & O(1)PN: \ 108.4 \ (109.8)\\ SePO(1): \ 109.6 \ (108.8) & O(2)PN: \ 103.6 \ (103.1)\\ SePO(2): \ 111.2 \ (111.9) & \\ dihedral \ angle \ C(1)C(2)C(4)C(5): \ -47.5 \ (-37.5) & \end{array}$ 



| Int2                     |                           |  |  |  |  |  |
|--------------------------|---------------------------|--|--|--|--|--|
| PSe: 2.130 (2.123)       | O(1)C(1): 1.341 (1.340)   |  |  |  |  |  |
| PN: 1.930 (1.927)        | O(2)C(2): 1.372 (1.371)   |  |  |  |  |  |
| PO(1): 1.832 (1.827)     | NC(3): 1.355 (1.353)      |  |  |  |  |  |
| PO(2): 1.716 (1.711)     | NC(4): 1.407 (1.406)      |  |  |  |  |  |
| NPSe: 100.6 (100.7)      | O(1)PN: 159.1 (159.0)     |  |  |  |  |  |
| SePO(1): 99.1 (99.1)     | O(2)PN: 86.8 (89.9)       |  |  |  |  |  |
| SePO(2): 121.1 (121.0)   |                           |  |  |  |  |  |
| dihedral angle: C(1)C(2) | C(4)C(5): -130.0 (-130.2) |  |  |  |  |  |

|                        | P                       |
|------------------------|-------------------------|
| P1 <b>12</b>           |                         |
| PSe: 2.120 (2.111)     | O(1)C(1): 1.358 (1.356) |
| PO(1): 1.746 (1.687)   | O(2)C(2): 1.358 (1.361) |
| PO(2): 1.746 (1.687)   |                         |
| SePO(1): 109.1 (111.0) | SePO(2): 109.1 (111.1)  |

dihedral angle: C(1)C(2)C(4)C(5): -13.6 (-13.0)

0(2)

S(1)

Fig. 6. The geometrical parameters of 1, 11, Int1, Int2, and 12 at the PW91/G03 (PW91/ADF) levels of theory.

| Table 1  |                                    |                |
|--|------------------------------------|----------------|
| Experimental and theoretical <sup>31</sup> P chemical shifts | , $\delta$ (in ppm) and $J_{P-Se}$ | values (in Hz) |

|                                   | Substrate <b>1</b> |                   | Anionic substrate <b>11</b> (R1) |                   | Int1 |            | Int2 |                   | <b>12</b> (P1) |                   |
|-----------------------------------|--------------------|-------------------|----------------------------------|-------------------|------|------------|------|-------------------|----------------|-------------------|
|                                   | δ                  | J <sub>P-Se</sub> | δ                                | J <sub>P-Se</sub> | δ    | $J_{P-Se}$ | δ    | J <sub>P-Se</sub> | δ              | J <sub>P-Se</sub> |
| Expt                              | 77.9               | 1018              | 59.8                             | 880               |      |            |      |                   | 120.9          | 875               |
| PW91/ADF                          | 105                | -1040             | 92                               | -925              | 118  | -987       | 124  | -871              | 179            | -891              |
| mPW1PW91/G03 (gas-phase)          | 118                | _                 | 100                              | _                 | 133  | _          | 59   | _                 | 212            | —                 |
| mPW1PW91/G03 (CH <sub>3</sub> CN) | 120                | _                 | 94                               | _                 | 133  | _          | 57   | _                 | 211            | _                 |
| mPW1PW91/G03 (THF)                | 119                | _                 | 95                               | _                 | 133  | -          | 57   | —                 | 211            | _                 |

<sup>a</sup> Chemical shifts are calculated with respect to the computed H<sub>3</sub>PO<sub>4</sub> absolute values=295 ppm (PW91/ADF); 303 ppm (mPW1PW91/G03 in gas-phase); 300 ppm (mPW1PW91/G03 in THF). Experimental value=328 ppm.

a higher stability, with **TS2** around 9 kcal/mol over the reactant asymptotes. It turns out to be quite apparent that the first stage of the reaction is the rate-determining step. However, the differences of energy for the **TS1** and **TS2** in solvent are rather moderate ( $\Delta E$ =0.58 kcal/mol), casting doubt over such a postulate. The solvent effects (solvation of anionic species) increase differences in the

potential energies of **TS1** and **TS2** ( $\Delta E \sim -1$  kcal/mol in a gas phase versus 5 kcal/mol in MeCN), corroborating a strong but multifaceted stabilization of ionic **TS1/TS2**. Experimental data support this interpretation, because in the case of the *PN*(*O*)  $\rightarrow$  *P*(*S*)*O* reaction we have not observed stable anions accompanied by much less stable species resonating at higher field.

#### Table 2

| $Calculated (PW91/ADF) Collections to I_{P-S_{P}} values (III \Pi Z)$ |
|---|
|---|

|                      | DO <sup>a</sup> | PSO <sup>b</sup> | FC+SD <sup>c</sup> | Total J <sub>P-Se</sub> |
|----------------------|-----------------|------------------|--------------------|-------------------------|
| Substrate 1          | 0.17            | -134.9           | -905.2             | -1040                   |
| Anionic substrate 11 | 0.17            | -126.6           | -798.8             | -925                    |
| Int1                 | 0.20            | -146.2           | -914.2             | -987                    |
| Int2                 | 0.18            | -135.0           | -736.2             | -871                    |
| 12 (P1)              | 0.15            | -135.5           | -755.6             | -891                    |

<sup>a</sup> Diamagnetic orbital contribution.

<sup>b</sup> Paramagnetic orbital contribution.

<sup>c</sup> Fermi-contact+spin-dipolar contribution (FC and SD contributions cannot be separated in this formalism).

The resulting major difference in mechanism proposed before, and the one appearing from the reported theoretical calculations at this level of approximations, is manifested in a consecutive rather than simultaneous break of the P–N and P–S bonds. The decomposition of the **TS2** proceeds in the way of the advanced P–N bond breaking followed by the P–S breaking. The structure of the **TS3** for the  $PN(Se) \rightarrow P(S)O$  reaction already has a tetracoordinate structure with the P–N bond split.

In conclusion, the reported studies provide additional information on the mechanism of the  $PN \rightarrow PX$  (O, S, Se) conversion, giving for the first time a comparison of the experimental results involving various temperature NMR studies and theoretical DFT studies. The potential surfaces allow for identification of the majority of the previously postulated intermediates and mark several well-defined transition states.

## 4. Experimental section

## 4.1. General

Reactions were carried out under a positive pressure of dry argon. Solvents and reagents were purified according to standard laboratory techniques and distilled directly into reaction vessels. Column chromatography and TLC analyses were performed on silica gel, and silica gel HP TLC precoated F<sub>254</sub> plates, respectively. NMR spectra were recorded on a Bruker Avance DRX 500 spectrometer, operating at 500.13 MHz (<sup>1</sup>H), and 202.46 MHz (<sup>31</sup>P). Chemical shifts ( $\delta$ ) are reported relative to TMS (1H) and 80% H<sub>3</sub>PO<sub>4</sub> (<sup>31</sup>P) as external standards. Mass spectra were recorded on a Finnigan Mat 95 (NBA, Cs<sup>+</sup> gun operating at 13 keV).

# 4.2. 2-Aniline-2-seleno-1,3,2-benzodioxaphospholane (1)

A solution of 2-chloro-1,3,2-benzodioxaphospholane (0.88 g, 0.05 mol) was added dropwise to a suspension of selenium (3.95 g, 0.05 mol) and aniline (10 mL, 0.11 mol) in dry toluene (40 mL) under argon and was sealed via a Teflon gauge. The reaction mixture was stirred at 130 °C for 3 days (<sup>31</sup>P NMR, 96%). After exhaustive extraction with 0.05 M citric acid followed by water, drying with MgSO<sub>4</sub> and concentration, a viscous liquid was dissolved in CH<sub>2</sub>Cl<sub>2</sub>, precipitated from toluene, and **1** obtained as white amorphous solid (13.94 g, 90%). *R*<sub>f</sub> (CHCl<sub>3</sub>/EtOH, 95:5 v/v) 0.60; MS Cl *m*/*z* 312.1 (M+2), 232.1 (100) (M–Se), 248.1 (M–Se+O), 450 (M+pyrocatechol) (requires C<sub>12</sub>H<sub>10</sub>O<sub>2</sub>N<sub>1</sub>P<sub>1</sub>Se<sub>1</sub> 310.962);  $\delta_P$  (C<sub>6</sub>D<sub>6</sub>) 77.8 (<sup>1</sup>*J*<sub>P–Se</sub> 1018 Hz).

# 4.3. 2-Hydroxy-2-seleno-1,3,2-benzodioxaphospholane (5)

Product **1** product was dissolved in chloroform and poured on a silica column under argon. Column chromatography was performed using chloroform as an eluent. Compound **5** was collected from the column major product (yield >80%, <sup>31</sup>P NMR  $\delta$  65.2 ppm, <sup>1</sup>J<sub>PSe</sub>=915 Hz) as anilinium salt. Compound **5** was crystallized from

benzene, and the X-ray analysis was performed.<sup>8</sup> The structural parameters obtained for the structure of **5** (details in Supplementary data) were used in molecular calculations.

## 4.4. 2-Aniline-2-thio-1,3,2-benzodioxaphospholane (4)

A solution of 2-chloro-1,3,2-benzodioxaphospholane (0.88 g, 0.05 mol) was added dropwise to a suspension of sulfur (1.6 g, 0.05 mol) and aniline (10 mL, 0.11 mol) in dry toluene under argon and was sealed via Teflon gauge. The reaction mixture was stirred at room temperature overnight. After extraction with a 5% solution of hydrochloric acid, drying with MgSO<sub>4</sub>, and concentration, a crude oily product was purified by means of silica gel chromatography (CHCl<sub>3</sub>) to give pure **4** as white amorphous solid after vacuum concentration (2.23 g, 85%).  $R_f$  (CHCl<sub>3</sub>/EtOH, 95:5 v/v) 0.63; MS Cl m/z 264.1 (M), 232.1 (M–S), 173.1, 306.2 (requires C<sub>12</sub>H<sub>10</sub>O<sub>2</sub>N<sub>1</sub>P<sub>1</sub>S<sub>1</sub> 263.0168);  $\delta_P$  (C<sub>6</sub>D<sub>6</sub>) 77.03;  $\delta_H$  (C<sub>6</sub>D<sub>6</sub>) 7.36 (2H, d, *J* 7.93) 7.35 (2H, *J* 7.81), 7.12 (2H, *J* 7.81), 6.87, 6.92 (m, 4H).

# 4.5. Low temperature studies by <sup>31</sup>P NMR

Low temperature experiments were performed in DMF with toluene- $d_8$  as internal standard added (5:1 v/v). The reagents were frozen gradually in layers in NMR tubes, sealed with septa under argon, and frozen in liquid nitrogen. The tubes were warmed up slowly to -60 °C in NMR machine and spectra were registered every 20 °C.

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## Supplementary data

An ORTEP drawing with selected bond parameters for **5**, variable temperature <sup>31</sup>P NMR spectra for **1**, and details on theoretical calculations. Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2012.04.081.

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