Chalcogens

Chalcogen-Transfer Rearrangement: Exploring Inter- versus Intramolecular P–P Bond Activation

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Dedicated to Prof. Dr. Dr. h.c. mult. Herbert W. Roessler on the occasion of his 85th birthday

Abstract: tert-Butyl-substituted diphospha[2]ferrocenophane has been used as a stereochemically confined diphosphane to explore the addition of O, S, Se and Te. Although the phosphanylchalcogane has been obtained for tellurium, all other chalcogens give diphosphane monochalcogenides. The latter transform via chalcogen-transfer rearrangement to the corresponding diphosphanylchalcoganes upon heating. The kinetics of this rearrangement has been followed with NMR spectroscopy supported by DFT calculations. Intermediates during rearrangement point to a disproportionation/synproportionation mechanism for the S and Se derivatives. Cyclic voltammetry together with DFT studies indicate ferrocene-centred oxidation for most of the compounds presented.

Introduction

Chalcogen transfer is a fundamental reaction in molecular chemistry and chalcogenophosphoranes (phosphine chalcogenides) are well established reagents for this purpose.[1] Although the preparation of phosphorus sulfides, as an example, is known since centuries, mechanistic details on how chalcogen atoms are transferred are still quite limited with some light shed by a study addressing the oxidation of white phosphorus with sulfur in the melt and at low temperature under thermal and photochemical conditions.[2] The scenario is complicated by initial chalcogen addition to either a phosphorus lone pair, or insertion into a P–P bond, potentially followed by subsequent interconversion via chalcogen migration proceeding intra- or intermolecularly (Scheme 1). Diphosphanes and diphosphane monochalcogenides are suitable model compounds for the study of such processes featuring a phosphorus lone pair as well as a P–P bond. For the case of sulfur, diphosphane monosulfides have been obtained via desulfurization of diphosphane disulfides,[3] oxidation of diphosphanes with elemental chalcogen,[4,5] or synproportionation of diphosphanes and diphosphane disulfides.[6] For the heavier chalcogen selenium, the corresponding diphosphane monoselenide was reported using the oxidation route,[6] and via metathesis of metal selendie and halophosphanes.[7,8] In a comprehensive study,[9] the steric influence on the relative ratio of the isomeric diphosphane monochalcogenides A and diphosphanylchalcogenes B has been explored for Ch = S, Se and Te, including the thermal conversion A → B which had been studied independently for Ch = O before.[10] The aspect of ring-strain on this transformation has been demonstrated elegantly for an o-carborane bridged diphosphane with Ch = Se.[11] While diphosphanylchalcogane isomer B is observed exclusively for Ch = Te,[11] the opposite is true for oxygen, where diphosphane monochalcogenide A is dominant, except for stereo-electronically unique organofluoro substituents.[11]

Based on previous results,[12] we considered tert-butyl substituted diphospha[2]ferrocenophane 1 as suitable diphosphane to study chalcogen-transfer reactions as it combines two stereoogenic P centres with lone pairs and a non-polar >P–P< bond. This compound is available as a single diastereomer with trans orientation of the tert-butyl groups adjacent to the P-stereogenic centres,[13] which should allow facile monitoring of epimerization via 31P NMR spectroscopy. Here we report our investigation concerning addition vs. insertion of chalcogen...
Results and Discussion

As a starting point of our investigation an improved synthesis of diphospha[2]ferrocenophane 1 has been developed furnishing analytically pure 1 by simple recrystallization in good yields (70%). Our approach employs oxidative P-P bond formation from the corresponding bisphosphanide using various oxidants (SiBr₄, CCl₄, CHCl₃, CHBr₃, PbCl₂) out of which PbCl₂ gave best results (Scheme 2). The advantage over a published route via reductive P-P bond formation accompanied by formation of by-products, is the ease of purification requiring no column chromatography as in the previous method,[13]

To explore whether one chalcogen atom (Ch = O, S, Se, Te) can be transferred selectively to diphosphane 1 by stoichiometric control, we employed reagents containing the respective chalcogen–chalcogen bonds. While H₂O₂ or tert-butyl hydroperoxide, S₈ and grey selenium furnish cleanly monooxidized diphosphane monochalcogenides 2a–c at room temperature, no reaction is observed with elemental tellurium under these conditions (Scheme 3). Nevertheless, at elevated temperature partial oxidation of 1 by tellurium can be observed (33% yield besides unreacted 1). Unlike for the other chalcogens, oxidation of 1 with tellurium leads exclusively to the ring expanded telluradiphospha[3]ferrocenophane 3d.

Upon monooxidation, the ³¹P NMR chemical shift of 20.6 ppm in 1,[13] changes to lower field for the tetracoordinate phosphorus atom in 2, while its trivalent counterpart is shifted to higher field (Table 1). Chemical inequivalence of the ³¹P nuclei in 2 entails signal splitting, for which the value of ¹JPP increases with the size of the chalcogen (Table 1). For 2c the ⁷⁷Se chemical shift at −311.7 ppm shows coupling to the directly bonded tetracoordinate and the trivalent phosphorus atoms (¹JSeP = 725 Hz, ¹JSeP = 30 Hz). Identity and purity of the above mentioned monooxidized diphosphanes was further corroborated by ¹H, ¹³C NMR, mass spectrometry and elemental analysis. Single crystals suitable for X-ray diffraction have been obtained for 2a,b (Figure 1). Remarkably the P-P bond lengths, 2.240(3) Å in 2a and 2.246(2) Å in 2b are almost identical to the one in non-oxidized 1.[13a] Compared with the latter, the tetracoordinate phosphorus

![Scheme 1](image1.png)

![Scheme 2](image2.png)

![Scheme 3](image3.png)

Table 1. ³¹P NMR chemical shifts and coupling constants of 2a–c.

|        | ³¹P (ppm) | ¹JPP [Hz] |
|--------|-----------|-----------|
| 2a     | 7.3       | 79.6      |
| 2b     | 15.6      | 86.2      |
| 2c     | 18.3      | 71.3      |

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Molecular structure of 2a (left) in the solid state. Ellipsoids were shown at 30% (2a) or 10% (2b) probability. Selected bond lengths and angles of 2a: twist angle \( \delta = 19.5(6)^\circ \); bond lengths: \( \text{P}1-\text{P}2 \) 2.240(3) Å, \( \text{P}1-\text{O}1 \) 1.487(6) Å, \( \text{P}1-\text{C}_{\text{Bu}} \) 1.858(8) Å, \( \text{P}2-\text{C}_{\text{Bu}} \) 1.884(8) Å; 2b: twist angle \( \delta = 20.3(6)^\circ \); bond lengths: \( \text{P}1-\text{P}2 \) 2.246(2) Å, \( \text{P}1-\text{S}1 \) 1.965(2) Å, \( \text{P}1-\text{C}_{\text{Bu}} \) 1.863(7) Å, \( \text{P}2-\text{C}_{\text{Bu}} \) 1.881(8) Å.

atoms in 2a and 2b increase to adapt to the quasi-tetrahedral coordination geometry. The tilt angle \( \alpha \) slightly decreases in the series 1 (13.6(1)\(^\circ\)), 2a (11.9(4)\(^\circ\)) and 2b (12.8(3)\(^\circ\)) indicating further release of angular strain upon oxidation.

With an excess of the oxidation reagents mentioned above, twofold oxidation of 1 with chalcogenes can be achieved as well. The resulting product is identical regardless whether 1 or 2 are exposed to excess oxidant, which indicates a stepwise oxidation of 1 via 2 to 4 (Scheme 4). The transformation can be followed easily by \( ^{31}\text{P} \) NMR spectroscopy and product 4 shows a single resonance indicating two chemically equivalent phosphorus nuclei in 4. These resonances in the \( ^{31}\text{P} \) NMR spectra at 68.3 ppm (4a), 81.8 ppm (4b) and 65.6 ppm (4c) are de-shielded with respect to 1 but appear at slightly higher field than the respective tetracoordinate phosphorus nuclei in 2.

The resulting selenophosphorane 4c shows a resonance at \(-275.6\) ppm in the \( ^{77}\text{Se} \) NMR spectra showing couplings of \( J_{\text{PS}} \) 741 Hz and \( J_{\text{PS}} \) 17 Hz which is comparable to the values obtained for 2c.

The identity of 4a–c has been further corroborated by single crystal X-ray diffraction (Figure 2). In the series 4a–c, the tert-butyl groups are oriented to opposite sides of the [2]ferrocenophane ring adopting a \textit{trans} configuration. Remarkably, the P-P bond lengths 2.2516(9) Å in 4a, 2.2695(9) Å in 4b and 2.2793(16) Å in 4c are almost identical to the one in non-oxidized 1. The tilt angle \( \alpha = 11.0(1)^\circ \) (4a), 10.6(1)^\circ (4b), 12.0(2)^\circ (4c) is slightly lower than in 1 and 2 (v.s.).

Rearrangement

An interesting feature is observed for diphosphane monochalcogenides 2b,c which transform slowly into the respective di-phosphanylchalcogenes 3b,c upon heating. While this migratory insertion requires boiling mesitylene over two weeks in the case of sulfur compound 2b, its selenium analogue 2c rearranges more facile, at 120°C within few hours. Com-

**Figure 1.** Molecular structure of 2a (left) and 2b (right) in the solid state. Ellipsoids were shown at 30% (2a) or 10% (2b) probability. Selected bond lengths and angles of 2a: twist angle \( \delta = 19.5(6)^\circ \); bond lengths: \( \text{P}1-\text{P}2 \) 2.240(3) Å, \( \text{P}1-\text{O}1 \) 1.487(6) Å, \( \text{P}1-\text{C}_{\text{Bu}} \) 1.858(8) Å, \( \text{P}2-\text{C}_{\text{Bu}} \) 1.884(8) Å; 2b: twist angle \( \delta = 20.3(6)^\circ \); bond lengths: \( \text{P}1-\text{P}2 \) 2.246(2) Å, \( \text{P}1-\text{S}1 \) 1.965(2) Å, \( \text{P}1-\text{C}_{\text{Bu}} \) 1.863(7) Å, \( \text{P}2-\text{C}_{\text{Bu}} \) 1.881(8) Å.

**Scheme 4.** Formation of twofold oxidized 4 via oxidation of 2 (Ch = O (a), S (b), Se (c); i: 1 equiv \( \text{H}_2\text{O}_2 \), rt, 30 min (2a); 1/8 \( \text{S}_8 \) rt, overnight (2b); 1 equiv Se (grey), rt, overnight (2c); ii: 1 equiv \( \text{H}_2\text{O} \), rt, 30 min (4a); 1/8 \( \text{S}_8 \), 110°C, overnight (4b); 1 equiv Se (grey), rt, 6 h (4c)). [*Yields refer to the direct conversion of 1 with 2 equiv of the chalcogen source.*]
pounds 3b,c obtained by rearrangement of 2b,c, as well as 3 d, directly obtained by oxidation of 1 (v.s.), are formed in a stereospecific manner showing a single resonance in the $^{31}$P{[1H]} NMR spectra at 51.8 ppm (3 b), 54.6 ppm (3 c) and 42.0 ppm (3 d). The chemical equivalence of the tert-butyl phosphanyl groups in the $^{31}$P-NMR spectra is indicative for the meso-form with a cis configuration in which both substituents are pointing to the same side of the [3]ferrocenophane ring. The corresponding $^{77}$Se resonance of 3c at 156.2 ppm is drastically deshielded by more than 460 ppm upon ring expansion compared with 2c, while the $^{1}J_{SeP}$ coupling drops to 164 Hz. The tellurium expanded [3]ferrocenophane 3d shows a $^{125}$Te resonance at 157.0 ppm which is split into a triplet arising from $^{1}J_{125TeP}$ coupling. Two sets of satellites are found in the $^{31}$P{[1H]} NMR spectrum owing to the two $^{125}$Te ($^{1}J_{125TeP} = 263$ Hz) and $^{129}$Te ($^{1}J_{129TeP} = 318$ Hz) isotoxopoluges (Figure 3).

The findings for 3b–d in solution are corroborated for the solid state by single crystal X-ray crystallography. The P-Ch-P angles of 91.50(5)° in 3b, 86.48(3)° in 3c and 82.63(3)° in 3d are close to the values observed for P-E-P angles in divalent tetrylene adducts with [3]ferrocenophane scaffold (E = Si, Sn, Pb). The tilt angle ($\alpha$) shows values of 4.6(2)° (3b), 3.6(2)° (3c) and 2.9(2)° (3d) which is in a typical range for phosphorus rich [3]ferrocenophanes. For compounds 3b–d no intermolecular Ch–Ch interactions were observed (Figure 4).

In light of the thermally induced rearrangement of diphenyl monochalcogenides 2b,c → 3b,c, outlined above, we wondered, whether twofold oxidized compounds 4 would...
behave likewise (Scheme 5). Indeed, thiodiphosphorane 4b rearranges in a similar and stereospecific fashion to 5b. The transformation seems to be much more facile since it occurs at lower temperature (170 °C) and is completed after a few hours. The rearrangement of the selenodiphosphorane 4c proceeds accordingly yielding 5c. Surprisingly, the isomerization of 4c takes place at higher temperature (150 °C) compared with 2c. In contrast to the monooxidized phosphorane 2a which shows no rearrangement to the corresponding diphosphanylchalcogene, a rearrangement of twofold oxidized 4a to 5a could be observed at high temperature (190 °C) over a period of several days.

Upon rearrangement, the $^{31}$P NMR chemical shift of 4a (68.3 ppm), 4b (81.8 ppm) and 4c (65.6 ppm) changes to lower field for the tetracoordinate phosphorus atom (Table 2), which is even more deshielded than in 2a,b,c. As expected, their trivalent counterparts in 5 resonate at higher field with $^{3}$J_{PP} coupling constants in the range of 43–60 Hz (Table 2). These assignments are also consistent with $^{77}$Se NMR of 5c, showing a doublet of doublets at 366.6 ppm ($^{1}$J_{SeP} = 336 Hz and $^{3}$J_{SeP} = 180 Hz) and a doublet of doublets at −200.3 ppm ($^{1}$J_{SeP} = 783 Hz and $^{3}$J_{SeP} = 37 Hz), assigned to >P-Se–P= and ≡P=Se, respectively.

Single crystal X-ray diffraction of 5b and 5c (Figure 5) shows shorter P-Ch contacts for the chalcogenophosphorane unit (5b: 1.9487(6) Å (P1–S2), 5c: 2.1021(7) Å (P2–Se2)) as compared to the contacts associated with the bridging chalcogen atoms (2.1031(6) Å (P1–S1), 5b: 2.2552(6) Å (P1–Se1), 5c). These parameters are very close to the respective ones in 2, 3 and 4, as are the P-Ch-P angles (95.73(2)°, 5b; 93.61(2)°, 5c) indicating no significant ring strain in 5b,c.

**Mechanism**

To understand the above mentioned chalcogen-transfer rearrangement, we set out to explore the energetics of the reaction and its intermediates for the transformation 2→3, described above. Investigating the mechanism of the insertion with DFT methods, established that the process is slightly exothermic and in general 3 is more stable than 2. The energetic preference increases in the order a<b<c<d. (The calculated values vary between 11.3—(−30.5) kJ mol⁻¹, depending on the applied DFT functionals Table S4–S6 in the Supporting Information). Firstly, we considered a monomolecular reaction mechanism for the transformation 2b→3b as depicted in Scheme S1 in the Supporting Information. (Similar processes were calculated for 2c→3c and 2d→3d transformations, tabulated data in Table S4–S6 in the Supporting Information). The rate limiting step is the chalcogen insertion and the reaction barrier of this
step (190.8 kJ mol\(^{-1}\)) is comparable with the bonding energy of the P-P bond (\(-200\) kJ mol\(^{-1}\)). Similar mechanism and slightly lower barriers were obtained for the 4 \(\rightarrow\) 5 rearrangements (more details in the Supporting Information Scheme S4). It should be highlighted that these barriers should be thermally accessible at the reaction temperature (over 100 °C), but do not rule out other mechanistic pathways. Besides a hypothetic intramolecular rearrangement also a bimolecular mechanism needs to be considered. In the literature a concerted rearrangement has been proposed for the rearrangement of acyclic diphosphane monochalcogenide to bisphosphanylchalco-
gane.\(^{30}\) Unfortunately, all our attempts to localize the corresponding transition states for the concerted bimolecular rearrangements failed in our hands. Based on the optimized molecular structures, steric repulsion between the tert-butyl groups and the ferrocenem oieties precludes a concerted bimolecular mechanism showing no energetic preference over the monomolecular rearrangement outlined in Scheme S1.

In support of a stepwise (non-concerted) rearrangement, tracking the transformation 2b \(\rightarrow\) 3b via \(^{31}\)P-NMR spectroscopy revealed the transient occurrence of intermediate 5b along with desulfurized 1 in equal amounts. The identity of intermediate 5b has been confirmed by comparison with independently synthesized 5b (v.i.). Similarly, for the selenium transfer rearrangement 2c \(\rightarrow\) 3c, tracking the rearrangement by NMR spectroscopy confirmed 5c along with deselenised 1 as intermediates. Consistent with the proposed reaction pathway, comproportionation of isolated 5c and 1 afforded 3c together with 2c, which were formed in equal amounts. Therefore, we conclude a disproportionation/synproportionation type mechanism for the chalcogen-transfer rearrangement under discus-
sion (Scheme 6). The bimolecular nature of the rate determining step of this non-concerted chalcogen-transfer rearrangement was established by NMR studies, running the reaction 2c \(\rightarrow\) 3c at different concentrations which confirmed a second-order kinetics for selenium transfer (Figure 6).

To enlighten the chalcogen-transfer rearrangement also the temperature dependence of 2c \(\rightarrow\) 3c was tracked by \(^{31}\)P-NMR (Figure 6), which allows us to determine the power law (second order reaction) and rate constants \(K_T\) as 0.75(2) \(x\) \(10^{-4}\) L mol\(^{-1}\) s\(^{-1}\) (\(T = 110\) °C); 1.89(2) \(x\) \(10^{-4}\) L mol\(^{-1}\) s\(^{-1}\) (\(T = 120\) °C); 2.34(3) \(x\) \(10^{-4}\) L mol\(^{-1}\) s\(^{-1}\) (\(T = 130\) °C); 5.82(3) \(x\) \(10^{-4}\) L mol\(^{-1}\) s\(^{-1}\) (\(T = 140\) °C).

Scheme 6. Disproportionation/synproportionation mechanism for chalcogen-transfer rearrangement 2 \(\rightarrow\) 3 (Ch = S (b), Se (c)).

Figure 6. Concentration dependence of 2c \(\rightarrow\) 3c at two different starting concentrations of 2c (\(T = 120\) °C; left). Temperature dependence of the rearrange-
ment 2c \(\rightarrow\) 3c over time with a starting concentration \(c_0\) = 0.157 mol L\(^{-1}\) (right).
10^-4 \text{ L mol}^{-1}\text{s}^{-1} (T = 140^\circ\text{C}) for the selenium transfer rearrangement. Plotting ln(κ) against 1/T results in a linear relation, which allows the determination of the activation energy (E_A \approx 83(\pm 13) \text{ kJ mol}^{-1}) from the slope of the linear regression (Figure S10, the Supporting information).

The suggested non-concerted bimolecular mechanism was investigated computationally as well. We have considered different pathways (more details in the Supporting Information) and generally it could be established that, the chalcogen transfer steps exhibit moderate barriers (\Delta G^\ddagger = 57.7–69.0 \text{ kJ mol}^{-1}) for Ch=Se, which is comparable with the experimentally obtained value and the bimolecular nature of the rate limiting step. On the other hand, it should be noted that in all investigated cases the chalcogen insertion into the P-P bond remain over 160 \text{ kJ mol}^{-1} (Scheme S4 in Supporting Information), which is not consistent with our experimental observations.

To resolve this ambiguity, further calculation and experiments were carried out. TD-DFT calculations indicate electron transfer from the lone pairs of the chalcogens towards the P-P antibonding orbital in case of 2bc and 4bc, which results in elongation of the P-P bond. Therefore, possible photoactivation cannot be excluded. Despite the promising DFT results, running the reaction 2c \rightarrow 3c at different temperatures under exclusion of light (brown glass NMR tubes; Figure S11, the Supporting Information) reveal no significant influence by light and the determined value of the activation energy (E_A = 76 (\pm 3) \text{ kJ mol}^{-1}) is comparable with the prior one. Also running the reaction 2c \rightarrow 3c at room temperature, but under illumination with UV-light (Hg-lamp, 15 W) shows no [3]ferrocenophane formation after several hours of illumination.

Hypothetically the oxidant properties of chalcogens, may furnish oxidation of the ferrocene unit which subsequently may undergo electron transfer with the neighbouring diphosphane unit, thus giving rise to radical species even in the absence of light. Therefore, we explored the redox properties of central compounds of this investigation by cyclic voltammetry (CV). In the proposed disproportionation/synproportionation mechanism (Scheme 6) diphosphane 1 is oxidized by 5, therefore we explored the electrochemical oxidation behaviour of 1 as a starting point. Diphosphane 1 shows two distinct oxidation events with peak potentials at 0.29(1)V and 0.97(1)V (vs. Fc^-/Fc; blue line in Figure S1). The first current response shows reversible redox behaviour, if the voltage sweep is reverted before the second redox process. The second current response is reversible as well. However, with decreasing sweeping rate upon going through both redox processes in a single potential sweep, the nature of both processes and the first redox process in particular becomes irreversible in the reduction sweep (Figure S1). As iron or phosphorus centred oxidation is known to be feasible in related compounds,\textsuperscript{12b,15a} DFT calculations were performed where the calculated spin density (at B3LYP/6-311G**//B97XD/6-311+G**) of 1 is localized at the ferrocene unit. Similarly, the CVs of chalcogeno and dichalcogeno phosphoranes 2a-c and 4a-c have been recorded (Figures S2–3 and Figure S5, The Supporting Information), indicating reversible iron centred oxidation as the primary redox event for most compounds (2a: 0.43(2)V; 4a: 0.54(1)V; 2b: 0.48(1)V; 4b: 0.61(1)V; all vs. Fc^-/Fc). The assignment to iron centred oxidation is in accordance with the calculated spindensity of the corresponding radical cations. An exception are selenophosphoranes 2c and 4c showing irreversible electro-chemical responses for the oxidation (Figure S2 and S3) The reason of this observation can be explained with the increased energy level of the lone pairs of the selenium (compared to S or O), which have more significant contribution to the HOMO, than the ferrocene unit (Figure S7). The impact of the rearrangement 2 \rightarrow 3 on the electronic situation of the ferrocene unit may also be assessed by CV for the sulfur species where the ferrocene-based oxidation peak potential changes from 0.48(2)V (vs. Fc^-/Fc) for 2b to 0.32(1)V (vs. Fc^-/Fc) for 3b. In agreement with the reversible process the Fe centre has significant contribution to the spindensity distribution of the corresponding radical 3b\textsuperscript{+}. Selenium analogue 3c reveals a ferrocene-centred oxidation at a peak potential of 0.33(1)V (vs. Fc^-/Fc) as well, which is reversible if the potential sweep is switched to reversed scan direction right after first oxidation by avoiding the oxidation of the P-Se-P scaffold. The tellurium analogue 3d shows a quasi-reversible ferrocene-based redox process at a peak potential of 0.37(2)V (vs. Fc^-/Fc), if the scan direction is switched right after the oxidation (Figure S4). In summary, the electrochemical investigation outlined above give no indication for redox based radical formation during oxidation and rearrangement of 1 or 2 with chalcogens. As a final check to prove or disprove the involvement of radical species in the thermal chalcogen-transfer rearrangement 2 \rightarrow 3 we performed the reaction in an EPR spectrometer at high temperature in a sealed EPR tube which did not give any indication for radical formation, unlike in other cases.\textsuperscript{12c}

**Conclusion**

We reported the addition versus insertion of chalcogens to a stereoechemically confined diphosphane 1 taking advantage of the ferrocenophane scaffold. The resulting diphosphane monochalcogenides 2 undergo a chalcogen-transfer rearrangement to the corresponding diphosphanylchalcogenes 3 for S and Se. The analogous behaviour is observed for twofold oxidized chalcogenodiphosphoranes 4 which rearrange stereospecifically to asymmetrically substituted 5. The mechanism of the chalcogen-transfer rearrangement was found to be bimolecular and non-concerted based on NMR and DFT studies. Detection and identification of by-products during rearrangement suggest a disproportionation/synproportionation mechanism for 2b \rightarrow 3b, while no evidence for radical intermediates or photoactivation could be found. The general relevance of our results emerges from the prevalence of P\textsuperscript{III}–P\textsuperscript{IV} units in all phosphorus allotropes with the competition of addition to P\textsuperscript{III} atoms versus insertion into P-P bonds being of utmost importance for P\textsubscript{2} activation or phosphorene functionalization being a surging topic in sustainable and materials chemistry. In future work we intend to generalize the stereospecific addition/insertion of other amphiphilic species into P–P bonds of moderately strain-ed oligophosphanes aiming at new routes to chiral organophosphanes.
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Conflict of interest

The authors declare no conflict of interest.

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