1,2σ³λ³-Oxaphosphetanes and Their P-Chalcogenides—A Combined Experimental and Theoretical Study

Florian Gleim 1,†, Antonio García Alcaraz 2,†, Gregor Schnakenburg 1, Arturo Espinosa Ferao 2,* and Rainer Streubel 1,†

1 Institut für Anorganische Chemie, Rheinische Friedrich-Wilhelms-Universität Bonn, Gerhard-Domagk-Straße 1, 53121 Bonn, Germany; f.gleim@uni-bonn.de (F.G.); gregor.schnakenburg@uni-bonn.de (G.S.)
2 Departamento de Química Orgánica, Facultad de Química, Campus de Espinardo, Universidad de Murcia, 30100 Murcia, Spain; antonio.garcia47@um.es
* Correspondence: artuesp@um.es (A.E.F.); r.streubel@uni-bonn.de (R.S.);
† These authors contributed equally to this work.

Abstract: Although 1,2σ³λ³-oxaphosphetanes have been known for a long time, the “low-coordinate” 1,2σ³λ³-oxaphosphetanes have only been known since their first synthesis in 2018 via decomplexation. Apart from ligation of this P-heterocycle to gold(I)chloride and the oxidation using ortho-chloranil, nothing on their chemistry has been reported so far. Herein, we describe the synthesis of new 1,2σ³λ³-oxaphosphetane complexes (3a–e) and free derivatives (4a–e), as well as reactions of 4a with chalcogens and/or chalcogen transfer reagents, which yielded the P-chalcogenides (14–16; Ch = O, S, Se). We also report on the theoretical results of the reaction pathways of C-phenyl-substituted 1,2σ³λ³-oxaphosphetanes and ring strain energies of 1,2σ³λ³-oxaphosphetane P-chalcogenides.

Keywords: phosphorous heterocycles; P-chalcogenides; strained molecules; oxidation; oxaphosphetanes

1. Introduction

Strained organic and inorganic ring systems [1] are of high interest, due to their special bonding situation and high reactivity; for example, oxetanes (I) (Figure 1) are important building blocks for the synthesis of more complicated molecules [2] and polymers [3]. The phosphorus-containing four-membered rings, the phosphetanes (II), drew attention because of their use as steering ligands in transition metal catalysis [4], and, more recently, their performance as organocatalyst [5–7]. The class of oxaphosphetanes can be regarded as an unusual combination of the features of oxetanes (I) and phosphetanes (II), which have been scarcely studied so far. Please note that isomeric 1,3-oxaphosphetanes (III) [8] and 1,2-oxaphosphetanes (IV) [9] do also exist.

![Figure 1.](https://www.mdpi.com/journal/molecules)

Figure 1. Oxetane (I), phosphetanes (σ³λ³ IIa, σ³λ⁵ IIb), 1,3-oxaphosphetanes (σ³λ³ IIIa, σ³λ⁵ IIIb), 1,2-oxaphosphetanes (σ³λ³ IVa, σ³λ⁵ IVb), 1,2σ³λ³-oxaphosphetane metal complexes (V), and 1,2σ³λ⁵-oxaphosphetanes (VI).

In case of III and IV, the higher substituted compounds have been investigated more often. For example, 1,3σ⁴λ⁵-oxaphosphetanes are available through intramolecular Mit-
sunobu reactions [8], and bi- and tricyclic 1,3σ₃λ₃-oxaphosphetanes have recently been proposed in the decomposition of HPfCO [10]. The high-coordinate 1,2σ³λ₃-oxaphosphetanes (IVb) were known for a long time as intermediates in the Wittig reaction, although they do not occur in all cases [9,11,12], or in the deoxygenation of epoxides [12,13]. Recent calculations by Espinosa show that they also occur in the phosphite-initiated reductive dimerization of ketones [14]. Until now, very few crystal structures of 1,2σ³λ₃-oxaphosphetanes (IVb) were reported [15–18].

In contrast, only the low-coordinate 1,2σ³λ₃-oxaphosphetanes (IVA) were proposed [19] for a long time, with no stable derivative known. We synthesized the corresponding κP-pentacarbonylmetal(0) complexes (M = Cr, Mo, W) (V) either through ring expansion of epoxides using highly reactive phosphinidenoid complexes [20,21], or ring formation through intramolecular nucleophilic attack. Recently, the free ligand was obtained [22] using a decomplexation strategy [23] for octahedral complexes [M(CO)₅L] by a combined thermal substitution with the chelating effect of bis(diphenylphosphino)ethane (DPPE). The first X-ray structure of a non-ligated 1,2σ³λ₃-oxaphosphetane (IVA) was also reported together with the P-oxidation using ortho-chloranil and the P-complexation of gold(I)chloride [22].

Similar to 1,2σ³λ₃-oxaphosphetanes (IVA), P-chalcogenides (VI) are rather elusive compounds. The 1,2-oxaphosphetane P-oxides (VI, E = O) were first reported by Regitz in 1973 [24], but it was later found by Inamoto that these products were in fact 3,4-dihydro-1H-2,3-benzoxaphosphorin 3-oxides [25]. In 1976, Inamoto proposed a 1,2-oxaphosphetane oxide as a reaction product of a phosphinidene oxide and trans-stilbene oxide [26]. However, the same author published a revised structure in 1991, showing that the product was in fact an acyclic secondary phosphate oxide [27]. In 1991, Hafez proposed an annulated 1,2-oxaphosphetane P-oxide-like structure for the photochemical reaction product of flavone with the Lawesson reagent. The product was only characterized by mass spectrometry, IR- and 1H-NMR spectroscopy, and elemental analysis, but as the publication lacks 13C- and 31P-NMR data and the four-membered ring bears no hydrogen atoms, this assignment might be incorrect [28]. In 1994, Okazaki reported the synthesis of a 1,2-oxaphosphetane P-oxide, kinetically stabilized through a bulky 2,4,6-triisopropylphenyl group at phosphorus [29]. Regarding the 1,2-oxaphosphetane P-sulfides (VI, E = S), there is only one publication proposing 2-alkylthio-1,2-oxaphosphetane P-sulfides as the thermodynamically stable product of the reaction of 3-alkylamino-2-butenoic esters with phosphorus pentasulfide [30]. To the best of our knowledge, the 1,2-oxaphosphetane selenides and tellurides (VI, E = Se, Te) are unknown so far.

Herein, syntheses of new C⁴-substituted 1,2σ³λ₃-oxaphosphetanes, the mechanistic evaluation of this reaction for model compounds using DFT calculations, as well as efforts to access their P-chalcogenides (VI, E = O, S, Se, Te) are described.

2. Results

2.1. Synthesis and Spectroscopic Characterization of 1,2σ³λ₃-Oxaphosphetanes

Firstly, the protocol currently used for accessing 1,2-oxaphosphanes [21,22,31] is significantly improved. In the absence of 12-crown-4 the P-triphenylmethyl (trityl) substituted Li/Cl phosphinidene complex 1 reacted cleanly with epoxides 2a-d in THF yielding the oxaphosphetane complexes 3a,a′=3d,d′ (Scheme 1). The new complexes 3b,b′=d,d′ could be isolated as pairs of diastereomers (Table 1). Compounds 3a,a′=d,d′ were then treated with 1,2-bis(diphenylphosphino)ethane (DPPE) at 80 °C for two days. The formation of the desired products 4a,a′=d,d′ was shown by 31P[1H]-NMR spectroscopy (Scheme 1). For 31P[31P]-NMR parameters, as well as product ratios, see Table 2. For all 3b,b′=e,e′, 3e,e′,e′′, and 4b,b′=d,d′ diastereomeric pairs, the more highfield shifted 31P[1H]-NMR signal can be tentatively assigned to the cis-isomers and the downfield shifted signal to the trans-isomers, based on former calculations for 3a,a′ and 4a,a′ [22].
Table 1. Selected NMR spectroscopic data of 3a,a’–d,d’ measured in CDCl₃, chemical shifts in ppm, and coupling constants in Hz. See Supplementary Materials for more data and spectra.

|                 | 3a,a’       | 3b,b’       | 3c,c’       | 3d,d’       |
|-----------------|-------------|-------------|-------------|-------------|
| Ratio           | 51:49       | 50:50       | 50:50       | 48:52       |
| δ(P)            | 185.6/207.2 | 183.5/206.1 | 187.6/208.8 | 187.3/208.7 |
| δ(CH₂)          | 2.92/2.96   | 2.90/2.35   | 2.91/2.95   | 2.90/2.98   |
| δ(CH)           | 4.17/39.9   | 37.5/50.9   | 40.6/38.5   | 39.5/40.9   |
| 1](P-C)         | 18.3/21.7   | 21.5/18.5   | 18.3/21.4   | 21.5/8.3    |
| δ(CP₃)         | 68.0/67.2   | 67.1/67.8   | 67.2/67.9   | 67.1/67.9   |
| 2](P-C)         | 77.7/82.0   | 85.9/90.1   | 80.9/85.0   | 81.1/85.2   |

* Denotes second set of the magnetically non-equivalent CH₂-protons arising from C⁴-substituted regioisomers.

Table 2. ³¹P[¹H]-NMR spectroscopic data of 4a,a’–d,d’, chemical shifts in ppm, coupling constants in Hz.

|                 | 4a,a’       | 4b,b’       | 4c,c’       | 4d,d’       |
|-----------------|-------------|-------------|-------------|-------------|
| Ratio           | 42:58       | 34:66       | 39:61       | 18:82       |
| δ(P)            | 163.7/199.0 ¹ | 161.2/196.7 ¹ | 166.2/199.0 ² | 166.3/199.4 ³ |

¹ Measured in CDCl₃. ² Measured in C₆D₆. ³ Measured in n-pentane.

It should be noted that the change in isomer ratio from the complexes 3a,a’–d,d’ to the free 1,2-oxaphosphetanes 4a,a’–d,d’ can be attributed to the method of purification (extraction with n-pentane). At the end of the reaction, the isomer ratio closely resembles that of the starting material, the final difference arising from slightly different solubilities of the isomers in n-pentane.

Crystal structures of complexes 3b,b’–d,d’ were obtained (see ESI), but the change of C⁴-substituent did not lead to significant changes of bond lengths or angles compared to similar known compounds reported in the literature [21]. In the case of unligated species 4b,b’ (Figure 2) and 4c,c’ (see ESI), their crystal structures were obtained after recrystallization from n-pentane. The bond lengths of 4b,b’–c,c’ are very similar compared to their metal complexes 3b,b’–c,c’. The bonds of phosphorus change by less than 2%. The change of the dihedral angle of the ring system is more prominent; for example, for 3b,b’ the dihedral angles are approximately 150° (cis) and 170° (trans), whereas the trans form of 4b,b’ is nearly planar and the cis-form bent more strongly (around 130°).
Figure 2. Molecular structures of 1,2-oxaphosphetane 4b,b’ in the solid state. Hydrogen atoms are omitted and the thermal ellipsoids are set at the 50% probability level. Split layers C2A:C2 equals 33:67, C2′:A:C2′ equals 45:55. Selected bond lengths in Å, angles in degree, second entry corresponds to the crystallographic positions denoted with a dash: P-O 1.6792(14)/1.6803(13), P-C1 1.854(2)/1.849(2), P-C6 1.9229(19)/1.9148(18), O-C2 1.538(3)/1.542(3), O-C2A 1.451(6)/1.477(4), C1-C2 1.562(3)/1.599(4), C1-C2A 1.609(7)/1.552(5), O-P-C1 79.93(8)/80.07(8), C2-O-P 96.67(13)/97.70(13), C2A-O-P 88.0(3), 88.04(19), O-C2-C1 94.35(18)/92.7(2), O-C2A-C1 95.8(4)/97.3(3), C2-C1-P 89.05(14)/89.23(14), and C2A-C1-P 77.6(2)/80.03(19).

As in the case of the P-bis(trimethylsilyl)methyl substituted phosphinidenoid complex, the reaction of 1 with styrene oxide (2e) did not lead to the C4-, but preferentially to the C3-substituted 1,2-oxaphosphetane complexes [31]. The synthesis of a phenyl-substituted 1,2-oxaphosphetane was also attempted via reaction of 1 with the above mentioned oxirane derivative (2e), hoping to profit from the huge steric demand of the trityl group. However, this reaction led to a mixture of four isomers, the diastereomeric pairs of the C4-(3e,e’) and C3-substituted complexes (3e*,e**) (Scheme 2), whose NMR data and ratios are collected in Table 3. The assignment of the 31P{1H}-NMR chemical shifts to the C3- and C4-substituted regioisomers is based on the P-bis(trimethylsilyl)methyl substituted case, where only the C3-substituted regioisomers are formed (proven by crystal structures), and where it is shown that they are downfield shifted in comparison to other C4-substituted derivatives [31]. Unfortunately, the mixture of 3e,e’ and 3e*,e** could not be separated using column chromatography, even at a lower temperature.

Scheme 2. Synthesis of C-phenyl substituted 1,2-oxaphosphetane complexes 3e,e’ and 3e*,e**.

Table 3. Selected NMR spectroscopic data of 3e,e’ and 3e*,e**, measured in the reaction solution, chemical shifts in ppm, and coupling constants in Hz.

| Ratio | 3e | 3e’ | 3e* | 3e** |
|-------|----|-----|-----|------|
| δ(P)  | 40 | 45  | 10  | 5    |
| δ(CH2)| 191.5 | 210.9 | 237.3 | 244.9 |
| nJ(P-C)| 39.7 | 40.4  | 75.9  | 76.2 |
|       | 18.8 | 21.7  | 13.1  | 13.6 |
2.2. DFT-Based Mechanistic Proposal

Quantum chemical calculations were performed to provide further insights into mechanistic aspects of the formation of C-phenyl-substituted 1,2-oxaphosphetanes 3e, e' and 3e*, e''. For the sake of computational economy, a methyl group (instead of trityl) was used as P-substituent in the Li/Cl phosphinidenoid moiety. Additionally, diethylene glycol dimethyl ether (DEGDME) was used as a model to provide an almost saturated coordination sphere for the Li cation. The approach of complex 5 to styrene oxide 2e (taking the S enantiomer for the model study) gave rise to a van der Waals complex 6, where the Li(DEGDME) group is coordinated to the epoxide O atom in a barrierless, thermodynamically favorable process, furnishing complex 7 (Scheme 3). Given the high oxophilicity of phosphorus centers, nucleophilic attack of the negatively charged P atom to the electron-deficient O atom in the cationic part was first studied. By elimination of the solvated LiCl salt 8, terminal phosphinidene-epoxide adduct 9 was formed in a markedly endergonic transformation, for which a TS could not be located. The singularity of a terminal phosphinidene pentacarbonyltungsten(0) oxirane adduct was recently studied [32], showing the weakest O→P bond among the whole series of cyclic ethers adducts of phosphinidene complexes. In contrast, complex 9 displayed a strengthened P→O bond with similar bond strength descriptors values than those obtained when the O donor is dimethyl ether gOMe2 (Table S1). Elongation of the less activated, non-benzylic C-O bond of 9 gives exergonically styrene 10 and phosphinidene oxide complex 11 through a moderate barrier (18.41 kcal mol⁻¹). A similar result was found previously for a terminal phosphinidene molybdenum(0) thiirane complex, giving rise to ethylene and a side-on complexed phosphinidene sulfide [33]. On the contrary, P insertion into the benzylic C-O bond proceeds through a lower-energy TS (9.81 kcal mol⁻¹) affording 1,2-oxaphosphetane 12* (C³-substituted) in a markedly exergonic process.

![Scheme 3](image-url)

Scheme 3. Reaction of model Li/Cl phosphinidenoid complex 5 with (S)-styrene oxide 2e giving rise to 9 and its evolution through C-O bond cleavages. Computed ZPE-corrected energies (kcal mol⁻¹) for both minima and TS (marked with a ‡ superscript) at the CPCM/THF/CCSD(T)/def2-TZVPP(ecp) level, in brackets.

A more favorable pathway to obtain the desired products resulted from the direct nucleophilic attack of the P atom to the epoxide C atoms of 7 (Scheme 4). The attack at the more positively charged benzylic carbon (qN = 0.03 e) is slightly kinetically favored (ΔΔF₂₉₈ = 0.69 kcal mol⁻¹) (Figure 3), due to a higher C-O bond activation (WBI = 0.881, MBO = 0.778) and the low steric hindrance of the methyl group at the phosphanido moiety. Conversely, the attack to the non-benzylic carbon atom (qN = 0.10 e), with a comparatively strengthened C-O bond (WBI = 0.908, MBO = 0.945), leads to a more stable alkoxide 13.
(Figure 3). However, when a tert-butyl group is attached to phosphorus, the attack to the non-benzylic carbon is (slightly) kinetically favored (see ESI). Therefore, in the real system with a trityl group, an even more favorable non-benzylic C-O insertion would be expected, due to the high steric hindrance. The cyclization to form the four-membered 1,2-oxaphosphetanes proceeds in both cases through similar energy TSs. The most stable isomer 12 is obtained (initially as the van der Waals complex 8·12) through the slightly higher energy barrier process. The pathways leading to minor diastereomers 12′ and 12′′ were also computed (see ESI).

Scheme 4. Mechanistic proposal for the formation of 1,2-oxaphosphetanes 12 and 12b* from the direct nucleophilic attack of the P atom to the epoxide C atoms of 7.

Figure 3. Calculated (CPCMTHF/CCSD(T)/def2-TZVPP(ecp)) minimum energy profile for the conversion of 7 into 12 and 12*.

2.3. Synthesis of 1,2-Oxaphosphetane P-Chalcogenides

As the main goal of the study was to synthesize various 1,2σ4λ5-oxaphosphetane chalcogenide derivatives, the 42:58 mixture of 4-methyl-1,2-oxaphosphetane 4a,4a′ was used as a good case in point.
In order to target P-oxide derivatives, reactions of the mixture $4a,a'$ with various oxygen-transfer reagents were studied. Treating $4a,a'$ with propylene oxide or trimethylamine $N$-oxide in toluene at r.t. was not effective to convert $4a,a'$ into $14a,a'$. The use of tert-butylhydroperoxide or meta-chloroperoxybenzoic acid (mCPBA) led to unselective reactions; however, the reaction using iodosylbenzene (Scheme 5) led to the selective formation of 1,2-oxaphosphetane $P$-oxides $14a,a'$. The product was fully characterized by NMR spectroscopy, as well as ESI and APCI mass spectrometry. The $^{31}P$($^1$H)-NMR spectrum of the product solution showed two resonance signals of 62.1 ppm and 63.5 ppm, in a ratio of 66:34. This assignment fits well with the reported shift of the $P$-trisopropylphenyl substituted 1,2-$\sigma^4\lambda^5$-oxaphosphetane $P$-oxide ($\delta$ ($^{31}P[^1]H$) = 48.7 ppm [29]).

![Scheme 5](image)

To synthesize 1,2-$\sigma^4\lambda^5$-oxaphosphetane $P$-sulfide $15a,a', 4a,a'$ was treated with elemental sulfur in toluene at ambient temperature (Scheme 6). The reaction occurred selectively; $15a,a'$ was isolated via extraction from $n$-pentane and it was fully characterized by NMR spectroscopy and LIFDI mass spectrometry. $^{31}P[^1]H$-NMR chemical shifts of the isomers of $15a,a'$ were observed at 115.8 (40%) and 120.0 ppm (60%). These values are close to those reported for a 2,5-dihydro-1,2-benzoxaphosphole-2-sulfide (130.2 ppm [34]).

![Scheme 6](image)

Under the same reaction conditions, but with a slightly longer reaction time (2 d instead of 1 d), $4a,a'$ was treated with elemental (gray) selenium. The 1,2-oxaphosphetane-$P$-selenides $16a,a'$ (Scheme 6) were formed in a selective manner and isolated as 29:71 mixture in good yields by filtration, and excess selenium was removed. The $16a,a'$ mixture was fully characterized by NMR spectroscopy and LIFDI mass spectrometry. Its $^{31}P[^1]H$-NMR spectrum showed two resonance signals with selenium satellites at 116.1 ppm ($^1J$(Se,P) = 839.7 Hz) and 121.5 ppm ($^1J$(Se,P) = 846.4 Hz), corresponding to the two diastereomers of $16a,a'$. The $^{77}Se[^1]H$-NMR spectrum showed two doublets at $-10.7$ and 79.4 ppm. A comparison to the (acyclic) $tert$-butyl-ethoxyphenylphosphate-$P$-selenide[33] ($\delta$ ($^{31}P[^1]H$) = 111.0 ppm, $^1J$(Se,P) = 786.3 Hz) showed very similar values for the phosphorus chemical shifts and coupling constants, whereas the selenium resonances of $16a,a'$ are downfield-shifted (cf. $\delta$ ($^{77}Se[^1]H$) = $-350.3$ ppm [35]).

However, $4a,a'$ did not react with elemental tellurium or tributylphosphane-$P$-telluride (as transfer reagent) to form 1,2-oxaphosphetane-$P$-tellurides under the same conditions, nor by heating to $80\ ^\circ$C.

A comparison of the $^{13}C[^1]H$-NMR data of $4a,a'$, $14a,a'$, $15a,a'$, and $16a,a'$ (Table 4) reveals, for all chalcogenides, the $^1J$(PC$^{12}$) and $^2J$(PC$^H$) coupling constants are increased as expected when oxidizing $P$(III) to $P$(V). In the case of $14a,a'$, the $^1J$(PC$^{Ph_3}$) constant also
increases, whereas it decreases when going from 4a,a’ to 15a,a’ and then to 16a,a’. The decrease in the coupling constant hints at a change of the hybridization of phosphorus and, concomitantly, the bond angles due to increased steric bulk near the ring system.

Table 4. Selected NMR spectroscopical data of 4a,a’, 14a,a’, 15a,a’, and 16a,a’, chemical shifts in ppm, and coupling constants in Hz. See Supplementary Materials for more data and spectra.

|       | 4a,a’ | 14a,a’ | 15a,a’ | 16a,a’ |
|-------|-------|--------|--------|--------|
| δ(P)  | 163.7/199.0 | 62.1/63.5 | 115.8/120.0 | 116.1/121.5 |
| δ(CH₂) | 2.22/2.45 | 2.53/2.56 | 2.49/2.22 | 2.62/2.43 |
| δ(CH₂*) | 2.69/2.48 | 2.75/2.96 | 2.49/2.72 | 2.75/3.00 |
| δ(CH)   | 5.12/4.62 | 4.25/5.04 | 4.78/4.05 | 4.88/4.26 |
| δ(CH₂)  | 33.7/31.2 | 39.5/38.9 | 44.8/44.4 | 45.6/44.6 |
| 1J(P-C) | 13.6/7.9 | 60.8/64.0 | 51.5/49.8 | 44.6/43.5 |
| δ(CPh₃) | 63.4/62.9 | 65.6/66.2 | 70.4/69.8 | 70.4/69.8 |
| 1J(P-C) | 52.3/50.7 | 73.3/71.9 | 46.1/47.8 | 33.4/35.4 |
| δ(CH)   | 77.6/83.0 | 72.1/74.3 | 75.3/74.5 | 76.1/76.1 |
| 2J(P-C) | 4.6/2.2 | 20.2/20.2 | 19.4/19.9 | 19.4/19.4 |

1 Measured in CDCl₃. 2 Measured in C₆D₆. * Denotes second set of the magnetically non-equivalent CH₂-protons arising from C₁-substituted regioisomers.

2.4. Ring Strain Energy of Model 1,2-Oxaphosphetane Derivatives

To obtain further insight into the chemistry of the 1,2-oxaphosphirane chalcogenides, their ring strain energies (RSEs) were computed for model 1,2-oxaphosphetane derivatives VIa-e (Scheme 7) using suitable homodesmotic reactions (see ESI), as previously completed for related three- and four-membered heterocycles [36–44]. RSEs values (Table 5) slightly increase in the order VIa < VIb < VIC < VID < VIE, therefore regularly increasing for heavier P-chalcogenides and also reproducing the reported variation on moving from the σ³δ⁻¹,2-oxaphosphetane VIa to its P-oxide derivative VIb [22].

![Scheme 7. Model 1,2-oxaphosphetane-P-chalcogenides VIa-e studied computationally.](image)

Table 5. Computed CCSD(T)//def2-TZVPP(ecp)//PBEh-3c RSEs (in kcal mol⁻¹) for model compounds VIa-e.

|       | VIa   | VIb   | VIC   | VID   | VIE   |
|-------|-------|-------|-------|-------|-------|
|       | 18.95 | 19.57 | 19.93 | 20.35 | 20.59 |

3. Materials and Methods

3.1. Synthetic Details

The syntheses of all compounds were performed under an argon atmosphere, using common Schlenk techniques and dry solvents. All NMR spectra were recorded on a Bruker AVI-300 or a Bruker AV III HD Prodigy 500 spectrometer at 25 °C. The ¹H and ¹³C NMR spectra were referenced to the residual proton resonances and the ¹³C NMR signals of the deuterated solvents and ³¹P to 85% H₃PO₄ as external standards, respectively. Please check the ESI for further experimental details.
3.2. Computational Details

DFT calculations were performed with the ORCA electronic structure program package (version 4.2.1, created by Frank Neese, Max Planck Institut für Kohlenforschung, Mülheim/Ruhr, Germany) [45]. All geometry optimizations were run in redundant internal coordinates with tight convergence criteria, in the gas phase, and using Grimme’s dispersion-corrected composite PBEh-3c level [46]. For the mechanistic study, solvent (THF) effects were taken into consideration with the CPCM solvation method [47] as implemented in ORCA. For Mo [48] and Te [49] atoms, the [def2-ECP(28)] effective core potential (ECP) was used. Harmonic frequency calculations verified the nature of ground states or transition states (TS), having all positive frequencies or only one imaginary frequency, respectively. TS structures were confirmed by following the intrinsic reaction path in both directions of the negative eigenvector. From these optimized geometries, all reported data were obtained by means of single-point (SP) calculations using the more polarized def2-TZVPP basis set [50]. Reported energies include the Zero-point energy (ZPE) correction term at the optimization level. In the case of mechanistic aspects, final energies were obtained by means of double-hybrid-meta-GGA functional PW91PBE [51,52], using the RI [53–55] approximation for the MP2 correlation part, together with the RI-JK approximation for Coulomb and exchange integrals in the DFT part. Additionally, the latest Grimme’s semiempirical atom-pair-wise London dispersion correction D4 was included [56]. For RSE calculations, final energies were computed with the near-linear scaling domain-based local pair natural orbital (DLPNO) [57] method, to achieve coupled cluster theory with single-double and perturbative triple excitations (CCSD(T)) [58] using the def2-TZVPP basis set.

4. Conclusions

The new unligated 1,2\textsuperscript{3}λ\textsuperscript{3}-oxaphosphetanes 4a,\textsuperscript{a′–d′} were synthesized and characterized. As a good case in point, a mixture of 4a,\textsuperscript{a′} was used to investigate oxidation reactions, i.e., to access less (Ch = O) and/or unknown (Ch = S, Se) 1,2\textsuperscript{4}λ\textsuperscript{5}-oxaphosphetane P-chalcogenides. DFT calculations provided mechanistic insights into the formation of C-phenyl-substituted 1,2\textsuperscript{3}λ\textsuperscript{3}-oxaphosphetanes 3e,\textsuperscript{e′} and 3e,\textsuperscript{e′*} using model derivatives. Nucleophilic attack to non-benzylic carbon of styrene oxide 2e followed by cyclization seems to be the preferred pathway which explains the preferred formation of 3e,\textsuperscript{e′}. Ring strain energy calculations revealed the tendency to increase RSE values in going from 1,2\textsuperscript{3}λ\textsuperscript{3}- to 1,2\textsuperscript{4}λ\textsuperscript{5}-oxaphosphetane P-chalcogenides and among the latter from the lighter to the heavier chalcogens.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/molecules27103345/s1. General procedures, synthetic methods, and analytical data for 3a,\textsuperscript{a′–d′}, 3b,\textsuperscript{b′–d′}, 3c,\textsuperscript{c′–d′}, 3e,\textsuperscript{e′–d′}, 4b,\textsuperscript{b′–c′}, 4c,\textsuperscript{c′–d′}, 14a,\textsuperscript{a′–c′}, 15a,\textsuperscript{a′–c′}, and 16a,\textsuperscript{a′–c′}; Crystal structure data of 3b,\textsuperscript{b′–d′}, 3c,\textsuperscript{c′–d′}, 3b,\textsuperscript{b′–d′}, 4b,\textsuperscript{b′–c′}, and 4c,\textsuperscript{c′–d′}; Figures S1–S9: \textsuperscript{1}H- and \textsuperscript{13}C-\textsuperscript{1}{[\textsuperscript{1}H]}-NMR spectra of 3b,\textsuperscript{b′–d′}; Figure S10: \textsuperscript{31}P-\textsuperscript{1}{[\textsuperscript{1}H]}-NMR spectra of 3e,\textsuperscript{e′} and 3e,\textsuperscript{e′*}; Figures S11–S19: \textsuperscript{1}H-, \textsuperscript{13}C-\textsuperscript{1}{[\textsuperscript{1}H]}-, and \textsuperscript{31}P-\textsuperscript{1}{[\textsuperscript{1}H]}-NMR spectra of 4b,\textsuperscript{b′–d′}; Figures S20–S22: \textsuperscript{1}H-, \textsuperscript{13}C-\textsuperscript{1}{[\textsuperscript{1}H]}-, and \textsuperscript{31}P-\textsuperscript{1}{[\textsuperscript{1}H]}-NMR spectra of 14a,\textsuperscript{a′}; Figures S23–S25: \textsuperscript{1}H-, \textsuperscript{13}C-\textsuperscript{1}{[\textsuperscript{1}H]}-, and \textsuperscript{31}P-\textsuperscript{1}{[\textsuperscript{1}H]}-NMR spectra of 15a,\textsuperscript{a′}; Figures S26–S29: \textsuperscript{1}H-, \textsuperscript{13}C-\textsuperscript{1}{[\textsuperscript{1}H]}-, and \textsuperscript{31}P-\textsuperscript{1}{[\textsuperscript{1}H]}-NMR spectra of 16a,\textsuperscript{a′}; Table S1: O bond properties of complexes 9 and \textsuperscript{9}{[\textsuperscript{13}O]}Me\textsuperscript{2}; Table S2: C-O bond properties of 2e, 2e-Li(EGDME) and 9; Scheme S1: Mechanistic proposal for the formation of 1,2-oxaphosphetanes 12\textsuperscript{d} and 12\textsuperscript{b**} from the direct nucleophilic attack of the P atom to the epoxide C atoms of 7; Figure S30: Calculated (CPCM\textsubscript{THF}/CCSD(T)/def2-TZVPP(ecp)) minimum energy profile for the conversion of 7 into 12\textsuperscript{d} and 12\textsuperscript{b**}; Scheme S2: Nucleophilic attack of the P atom of 5\textsuperscript{Bu} to C atoms of styrene oxide 2e giving rise to 13\textsuperscript{Bu} and 13\textsuperscript{Bu*}; Figure S31: Calculated (CPCM\textsubscript{THF}/CCSD(T)/def2-TZVPP(ecp)) minimum energy profile for the conversion of 5\textsuperscript{Bu} + 2e into 13\textsuperscript{Bu} and 13\textsuperscript{Bu*}; Scheme S3: Homodesmotic reactions for RSE evaluation on derivatives 11a–e; Calculated structures.

Author Contributions: Conceptualization, A.E.F. and R.S.; methodology, F.G. and A.G.A.; validation, A.E.F. and R.S.; formal analysis, investigation, F.G. and A.G.A.; resources, R.S.; data curation, A.E.F. and R.S.; writing—review and editing, F.G., G.S., A.E.F. and R.S.; supervision, A.E.F. and R.S. All authors have read and agreed to the published version of the manuscript.
References

1. He, G.; Shynkaruk, O.; Lui, M.W.; Rivard, E. Small Inorganic Rings in the 21st Century: From Fleeting Intermediates to Novel Isolable Entities. Chem. Rev. 2014, 114, 7815–7880. [CrossRef] [PubMed]
2. Bull, J.A.; Croft, R.A.; Davis, O.A.; Doran, R.; Morgan, K.F. Oxetanes: Recent Advances in Synthesis, Reactivity, and Medicinal Chemistry. Chem. Rev. 2016, 116, 12150–12233. [CrossRef] [PubMed]
3. Klein, R.; Wurm, F.R. Aliphatic Polyethers: Classical Polymers for the 21st Century. Macromol. Rapid Commun. 2015, 36, 1147–1165. [CrossRef] [PubMed]
4. Marinetti, A.; Carmichael, D. Synthesis and Properties of Phosphatanes. Chem. Rev. 2002, 102, 201–230. [CrossRef]
5. Zhao, W.; Yan, P.K.; Radosevich, A.T. A Phosphetane Catalyzes Deoxygenative Condensation of α-Keto Esters and Carboxylic Acids via PIII/PV=O Redox Cycling. J. Am. Chem. Soc. 2015, 137, 616–619. [CrossRef]
6. Reichl, K.D.; Dunn, N.L.; Fastuca, N.J.; Radosevich, A.T. Biphilic Organophosphorus Catalysis: Regioselective Reductive Transposition of Allylic Bromides via PIII/PV Redox Cycling. J. Am. Chem. Soc. 2015, 137, 5292–5295. [CrossRef]
7. Nykaza, T.V.; Harrison, T.S.; Ghosh, A.; Putnik, R.A.; Radosevich, A.T. A Biphilic Phosphetane Catalyzes N–N Bond-Forming Cadogan Heterocyclization via PIII/PV=O Redox Cycling. J. Am. Chem. Soc. 2017, 139, 6839–6842. [CrossRef]
8. Kaboudin, B.; Haghighat, H.; Yokomatsu, T. Synthesis of a New Class of Phosphinic Acids: Synthesis of Novel Four-Membered Cyclic Oxaphosphatanes by Intramolecular Mitsunobu Reaction of Bis(α-hydroxyalkyl)phosphinic Acids. Synthesis 2011, 2011, 3185–3189. [CrossRef]
9. Wittig, G.; Geissler, G. Zur Reaktionsweise des Pentaphenylyphosphors und einiger Derivate. Justus Liebigs Ann. Chem. 1953, 580, 44–57. [CrossRef]
10. Hinz, A.; Labbow, R.; Rennick, C.; Schulz, A.; Goicoechea, J.M. HPCO—A Phosphorus-Containing Analogue of Isocyanic Acid. Angew. Chem. Int. Ed. 2017, 56, 3911–3915. [CrossRef]
11. Wittig, G.; Schöllkopf, U. Über Triphenyl-phosphin-methylene als olefinbildende Reagenzien (I. Mitteil). Chem. Ber. 1954, 87, 1318–1330. [CrossRef]
12. Vedejs, E.; Meier, G.P.; Snoble, K.A.J. Low-temperature characterization of the intermediates in the Wittig reaction. J. Am. Chem. Soc. 1981, 103, 2823–2831. [CrossRef]
13. Wittig, G.; Haag, W. Über Triphenyl-phosphinnmethylen als olefinbildende Reagenzien (II. Mitteil.1). Chem. Ber. 1955, 88, 1654–1666. [CrossRef]
14. Espinosa Ferao, A. On the Mechanism of Trimethylphosphine-Mediated Reductive Dimerization of Ketones. Inorg. Chem. 2018, 57, 8058–8064. [CrossRef]
15. Dieckbreder, U.; Lork, E.; Röschenthaler, G.-V.; Kolomeitsev, A.A. First P-trifluoromethylated ylides. Heterocot. Chem. 1996, 7, 281–284. [CrossRef]
16. Hamaguchi, M.; Iyama, Y.; Mochizuki, E.; Oshima, T. First isolation and characterization of 1,2-oxaphosphetanes with three phenyl groups at the phosphorus atom in typical Wittig reaction using cyclopropyldieneretriphenylphosphorane. Tetrahedron Lett. 2005, 46, 8949–8952. [CrossRef]
17. Kawashima, T.; Kato, K.; Okazaki, R. Synthesis, Structure, and Thermolysis of a 3-Methoxyacarbonyl-1, 2 θ5-oxaphosphetane. Angew. Chem. Int. Ed. Engl. 1993, 32, 869–870. [CrossRef]
18. Caughlan, C.N.; Ramirez, F.; Pilot, J.F.; Smith, C.P. Crystal and molecular structure of a four-membered cyclic oxyphosphorane with pentavalent phosphorus, PO2(C6H5)2(CF3)4C3H2. J. Am. Chem. Soc. 1971, 93, 5229–5235. [CrossRef]
19. Dianova, E.N.; Zabotina, E.Y.; Akhmethkhoava, I.Z.; Samuilov, Y.D. 5-Methyl-2-phenyl-1,2,3-diazaphosphole in reaction with 2,5-bis(methoxyacarbonyl)-3,4-diphenylcyclopentadiene. Zh. Obs. Khim. 1991, 64, 1063–1066. [CrossRef]
20. Kyri, A.W.; Schnakenburg, G.; Streubel, R. A novel route to C-unsubstituted 1,2-oxaphosphetane and 1,2-oxaphospholine complexes. Chem. Commun. 2016, 52, 8593–8595. [CrossRef]
21. Kyri, A.W. Investigations on 1,2-Oxaphosphetane Complexes. Ph.D. Thesis, University of Bonn, Bonn, Germany, 2017.
22. Kyri, A.W.; Gleim, F.; García Alcaraz, A.; Schnakenburg, G.; Espinosa Ferao, A.; Streubel, R. “Low-coordinate” 1,2-oxaphosphetanes—A new opportunity in coordination and main group chemistry. *Chem. Commun.* 2018, 54, 7123–7126. [CrossRef] [PubMed]

23. Espinosa Ferao, A.; Deschamps, B.; Mathey, F. Towards functional phospholide ions: Synthesis of a 3-ethoxycarbonyl derivative. *Bull. Soc. Chim. Fr.* 1993, 130, 695–699.

24. Regitz, M.; Scherer, H.; Illger, W.; Ecke, H. Detection of Alkylideneoxophosphoranes by Cycloaddition of Carbonyl Compounds. *Angew. Chem. Int. Ed. Engl.* 1973, 12, 1010–1011. [CrossRef]

25. Kawashima, T.; Inamoto, N. The Correct Structure of Cyclic Adducts of (Diphenylmethylene)oxophosphorane with Aromatic Aldehydes. *Bull. Chem. Soc. Jpn.* 1969, 42, 673–715. [CrossRef]

26. Nakayama, S.; Yoshifuji, M.; Okazaki, R.; Inamoto, N. Phosphinidenes and Related Intermediates. V. Reactions of Phosphinidenes with cis- and trans-Stilbene Oxides. *Bull. Chem. Soc. Jpn.* 1976, 49, 1173–1174. [CrossRef]

27. Kawashima, T.; Nakayama, S.; Yoshifuji, M.; Okazaki, R.; Inamoto, N. Revised Structure of 2-Cyclohexyl-3,4-diphenyl-1,2-oxaphosphetane 2-Oxide. *Bull. Chem. Soc. Jpn.* 1991, 64, 711–712. [CrossRef]

28. Hafez, T.S.; El-Khoshnieh, Y.O.; Mahran, M.R.; Atta, S.M.S. Organophosphorus Chemistry. 20. The Behaviour of Certain γ-Pyrone Derivatives toward 2,4-BIS-(4-Methoxyphenyl)-1,3,2-Dithiaposphetan-2,4-Disulphide (Lawesson Reagent). *Phosphorus. Sulfur. Silicon Relat.Elem.* 1991, 56, 165–171. [CrossRef]

29. Kawashima, T.; Takami, H.; Okazaki, R. Synthesis and Thermolysis of Tetracoordinate 1,2-Oxaphosphetanes Stabilized by Steric Protection. *Chem. Lett.* 1994, 23, 1487–1490. [CrossRef]

30. Dabrowska, U.; Dabrowski, J. IR-Spektren und Struktur von α-β-ungesättigten Carbonylverbindungen, XXI. Thione aus der Reaktion von Alkylaminocrotonestern mit Phosphorpentasulfid. *Chem. Ber.* 1976, 109, 1779–1789. [CrossRef]

31. Kyri, A.W.; Nesterov, V.; Schnakenburg, G.; Streubel, R. Synthesis and Reaction of the First 1,2-Oxaphosphetane Complexes. *Angew. Chem. Int. Ed.* 2014, 53, 10809–10812. [CrossRef]

32. Espinosa Ferao, A.; García Alcaraz, A.; Zaragoza Noguera, S.; Streubel, R. Terminal Phosphinidene Complex Adducts with Neutral and Anionic O-Donors and Halides and the Search for a Differentiating Bonding Descriptor. *Inorg. Chem.* 2020, 59, 12829–12841. [CrossRef] [PubMed]

33. Espinosa Ferao, A.; Streubel, R. 1,2-Thiaphosphetanes: The Quest for Wittig-Type Ring Cleavage, Rearrangement, and Sulfur Atom Transfer. *Inorg. Chem.* 2020, 59, 3110–3117. [CrossRef] [PubMed]

34. Kojima, S.; Sugino, M.; Matsukawa, S.; Nakamoto, M.; Akiba, K. First Isolation and Characterization of an Anti-Apicophilic Atom Transfer. *Inorg. Chem.* 2002, 41, 1487–1490. [CrossRef]

35. Kimura, T.; Murai, T. P-Chiral Phosphinolene Chlorides and Phosphinolacogenoselenenoic Acid Esters: Synthesis, Characterization, and Conformational Studies. *J. Org. Chem.* 2005, 70, 952–959. [CrossRef] [PubMed]

36. Rey, A.; Espinosa Ferao, A.; Streubel, R. Quantum Chemical Calculations on CHOP Derivatives—Spanning the Chemical Space of Phosphinidenes, Phosphaketenes, Oxaphosphetenes, and COP-Isomers. *Molecules* 2018, 23, 3341. [CrossRef]

37. Espinosa Ferao, A. Kinetic energy density per electron as quick insight into ring strain energies. *Tetrahedron Lett.* 2016, 57, 5616–5619. [CrossRef]

38. Streubel, R.; Faßbender, J.; Schnakenburg, G.; Espinosa Ferao, A. Formation of Transient and Stable 1,3-Dipole Complexes with P,Sc and P,PC Ligand Skeletons. *Organometallics* 2015, 34, 3103–3106. [CrossRef]

39. Villalba Franco, J.M.; Schnakenburg, G.; Sasamori, T.; Espinosa Ferao, A.; Streubel, R. Stimuli-Responsive Frustrated Lewis-Pair-Type Reactivity of a Tungsten Iminoazaphosphiridine Complex. *Chem.—A Eur. J.* 2015, 21, 9650–9655. [CrossRef]

40. Albrecht, C.; Schneider, E.; Engeser, M.; Schnakenburg, G.; Espinosa Ferao, A.; Streubel, R. Synthesis and DFT calculations of spirooxaphosphirane complexes. *Dalton Trans.* 2013, 42, 8897–8906. [CrossRef]

41. Espinosa, A.; Gómez, C.; Streubel, R. Single Electron Transfer-Mediated Selective endo- and exocyclic Bond Cleavage Processes in Azaphosphiridine Chromium(0) Complexes: A Computational Study. *Inorg. Chem.* 2012, 51, 7250–7256. [CrossRef]

42. Schulten, C.; von Frantzius, G.; Schnakenburg, G.; Streubel, R. Deoxygenation of isocyanates via transient electrophilic terminal phosphinidene complexes: Are strained P-heterocycles involved? *Heteroat. Chem.* 2011, 22, 275–286. [CrossRef]

43. Espinosa, A.; Streubel, R. Computational Studies on Azaphosphiridines, or How to Effect Ring-Opening Processes through Selective Bond Activation. *Chem.—A Eur. J.* 2011, 17, 3166–3178. [CrossRef] [PubMed]

44. Krahe, O.; Neese, F.; Streubel, R. The Quest for Ring Opening of Oxaphosphirane Complexes: A Coupled-Cluster and Density Functional Study of CH3PO Isomers and Their Cr(OC)3 Complexes. *Chem. Eur. J.* 2009, 15, 2594–2601. [CrossRef] [PubMed]

45. Neese, F. The ORCA program system. *Wiley Interdiscip. Rev. Comput. Mol. Sci.* 2012, 2, 73–78. [CrossRef]

46. Grimme, S.; Brandenburg, J.G.; Bannwarth, C.; Hansen, A. Consistent structures and interactions by density functional theory with small atomic orbital basis sets. *J. Chem. Phys.* 2015, 143, 54107. [CrossRef]

47. Barone, V.; Cossi, M. Quantum Calculation of Molecular Energies and Energy Gradients in Solution by a Conductor Solvent Model. *J. Phys. Chem.* A 1998, 102, 1995–2001. [CrossRef]

48. Andrae, D.; Häußermann, U.; Dolg, M.; Stoll, H.; Preuß, H. Energy-adjusted ab initio pseudopotentials for the second and third row transition elements. *Theor. Chim. Acta* 1990, 77, 123–141. [CrossRef]
49. Peterson, K.A.; Figgen, D.; Goll, E.; Stoll, H.; Dolg, M. Systematically convergent basis sets with relativistic pseudopotentials. II. Small-core pseudopotentials and correlation consistent basis sets for the post-d group 16–18 elements. *J. Chem. Phys.* 2003, 119, 11113–11123. [CrossRef]

50. Schäfer, A.; Huber, C.; Ahlrichs, R. Fully optimized contracted Gaussian basis sets of triple zeta valence quality for atoms Li to Kr. *J. Chem. Phys.* 1994, 100, 5829–5835. [CrossRef]

51. Goerigk, L.; Grimme, S. A thorough benchmark of density functional methods for general main group thermochemistry, kinetics, and noncovalent interactions. *Phys. Chem. Chem. Phys.* 2011, 13, 6670–6688. [CrossRef]

52. Goerigk, L.; Grimme, S. Efficient and Accurate Double-Hybrid-Meta-GGA Density Functionals—Evaluation with the Extended GMTKN30 Database for General Main Group Thermochemistry, Kinetics, and Noncovalent Interactions. *J. Chem. Theory Comput.* 2011, 7, 291–309. [CrossRef] [PubMed]

53. Weigend, F.; Häser, M.; Patzelt, H.; Ahlrichs, R. RI-MP2: Optimized auxiliary basis sets and demonstration of efficiency. *Chem. Phys. Lett.* 1998, 294, 143–152. [CrossRef]

54. Weigend, F.; Häser, M. RI-MP2: First derivatives and global consistency. *Theor. Chem. Acc.* 1997, 97, 331–340. [CrossRef]

55. Bernholdt, D.E.; Harrison, R.J. Large-scale correlated electronic structure calculations: The RI-MP2 method on parallel computers. *Chem. Phys. Lett.* 1996, 250, 477–484. [CrossRef]

56. Caldeweyher, E.; Bannwarth, C.; Grimme, S. Extension of the D3 dispersion coefficient model. *J. Chem. Phys.* 2017, 147, 34112. [CrossRef] [PubMed]

57. Riplinger, C.; Sandhoefer, B.; Hansen, A.; Neese, F. Natural triple excitations in local coupled cluster calculations with pair natural orbitals. *J. Chem. Phys.* 2013, 139, 134101. [CrossRef]

58. Pople, J.A.; Head-Gordon, M.; Raghavachari, K. Quadratic configuration interaction. A general technique for determining electron correlation energies. *J. Chem. Phys.* 1987, 87, 5968–5975. [CrossRef]