

#### Article

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# Oxophosphonium-alkyne cycloaddition reactions: reversible formation of 1,2-oxaphosphetes and six-membered phosphorus heterocycles

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phosphorus cations - phosphorus heterocycles - cycloaddition reactions - metathesis reactions - Lewis acids

**ABSTRACT:** While the metathesis reaction between alkynes and carbonyl compounds is an important tool in organic synthesis, the reactivity of alkynes with isoelectronic main group  $R_2E=0$  compounds is unexplored. Herein, we show that oxophosphonium ions, which are the isoelectronic phosphorus congeners to carbonyl compounds, undergo [2+2] cycloaddition reactions with different alkynes to generate 1,2-oxaphosphete ions, which were isolated and structurally characterized. The strained phosphorus-oxygen heterocycles open to the corresponding hetero-diene structure at elevated temperature, which was used to generate six-membered phosphorus heterocycles via hetero Diels-Alder reactions. Insights into the influence of the substituents at the phosphorus center on the energy profile of the oxygen atom transfer reaction were obtained by quantum chemical calculations.

#### Introduction

The metathesis reaction between carbonyls and alkynes is a powerful method for the synthesis of  $\alpha$ , $\beta$ -unsaturated ketones and has received much attention in the construction of heterocycles and in natural product synthesis.<sup>1-12</sup> This well-understood reaction involves an oxete intermediate which is unstable towards ring opening and the formation of the enone product (Scheme 1a).<sup>13</sup> Since carbonyl–alkyne [2+2] cycloadditions are orbitalsymmetry-forbidden in the ground state,<sup>14</sup> either photoirradiation<sup>15</sup> or the use of a catalyst<sup>16,17</sup> have been established as avenues to overcome the kinetic barriers. Nonetheless, the strained cyclic intermediate can be stabilized by electron withdrawing substituents, which has allowed the isolation and structural characterization of many oxete derivatives.<sup>18-22</sup>

In contrast to ketones, isoelectronic main group element E=O doubly bonded species are prone to spontaneous dimerization or polymerization and thus require kinetic stabilization. In 2012, Tamao and co-workers isolated the first heavy ketone analogue with a terminal oxygen atom, a germanone R<sub>2</sub>Ge=0.<sup>23</sup> Subsequent discoveries of stable silanones (R<sub>2</sub>Si=O),<sup>24-28</sup> an anionic oxoborane ([R<sub>2</sub>B=O]<sup>-</sup>)<sup>29</sup> and oxophosphonium ions  $([R_2P=O]^+)^{30}$  by the groups of 51 Filippou, Kato, Inoue, Rieger, Iwamoto, Aldridge and by us 52 extended this series of heavy ketones. While the chemistry 53 of these compounds has been extensively explored, [2+2] 54 cycloaddition reactions with alkynes leading to the heavy 55 oxete analogues have not yet been encountered. However, 56 beyond main group elements. Bergman and coworkers 57 discovered that oxido complexes of titanium and zirconium undergo cycloaddition reactions with alkynes to 58 give oxametallacyclobutenes I (Scheme 1b).<sup>31-33</sup> Unlike 59 60

oxetes, the four-membered metallacycles are formed reversibly and they exhibit a rich chemistry which predominantly involves insertion reactions into the metalcarbon bond.<sup>34–38</sup> Moreover, thermolysis of **I** in the absence of reactants leads to rearrangement reactions involving the cyclopentadienyl ligands or to the corresponding hydroxoacetylide **II**.<sup>33,39,40</sup>

Our recent success in synthesizing Lewis base-free oxophosphonium ions<sup>30</sup> has inspired us to explore whether they would undergo cycloaddition reactions with alkynes. Regarding the analogy to the carbonyl–alkyne metathesis, this reaction would either result in  $1,2\sigma^4\lambda^4$ -oxaphosphete four-membered rings or lead to the formation of 1-phospha-4-oxa-butadiene ions (Scheme 1c).

Given the importance of  $1, 2\sigma^5 \lambda^5$ -oxaphosphetanes **C** as intermediates in the Wittig reaction<sup>41,42</sup> and the rich chemistry of  $1,2\sigma^3\lambda^3$ -oxaphosphetanes **B** developed by the group of Streubel,<sup>43-48</sup> it is surprising that 1,2oxaphosphetes have not yet been isolated. Keglevich and co-workers postulated  $1,2\sigma^5\lambda^5$ -oxaphosphete intermediates in the reaction of phosphine oxides with the electrophilic particularly alkvne dimethylacetylenedicarboxylate.49 Mucsi and coworkers showed that these species are unstable towards ring opening reactions leading to stabilized phosphoniumylides.50 Recently the first example of a  $1,2\sigma^{3}\lambda^{3}$ -thiaphosphete **E** was synthesized by Ragogna and coworkers via transfer of a phosphinidene sulfide intermediate to an alkyne.<sup>51</sup> Herein, we report the reaction of oxophosphonium ions with alkynes that gives access to the first main group element heavy oxetes, namely  $1, 2\sigma^4 \lambda^4$ oxaphosphete ions. Studies on the reactivity of this species reveal analogies both to alkyne-carbonyl metathesis and to Environment the chemistry of oxametallacyclobutenes. In addition, computational methods were employed to elucidate the influence of the substituents at phosphorus on the energy profile of the reaction mechanism.

Scheme 1. a) Reaction of carbonyls with alkynes triggered by irradiation or catalysts (cat. = Lewis or Bronsted acid). b) Reaction of metallocene oxido complexes with alkynes. C) Reaction of oxophosphonium ions with alkynes to give  $1,2\sigma^4\lambda^4$ oxaphosphete cations. d) Examples of isolated fourmembered heterocycles: oxetane (A), 1,2oxaphosphetane (B, C), oxete (D), 1,2-thiaphosphete (E). Dipp = 2,6-diisopropylphenyl.

a) Carbonyl-alkyne metathesis



b) Bergman

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c) This work



#### **Results and Discussion**

Reaction of oxophosphonium salts with alkynes. We previously showed that the Lewis base-free oxophosphonium salts  $[(R^1)_2P=0][X]$   $(R^1 = 1,3-bis(2,6$ diisopropylphenyl)imidazolin-2-ylidenamino, [X]<sup>-</sup> = triflate [OTf]<sup>-</sup> or tetrakis[2,6-bis(trifluoromethyl)phenyl]borate  $[BArF_{24}]$ ) ([1][X]) can be prepared by reacting POCl<sub>3</sub> with two equivalents of R<sup>1</sup>-TMS via elimination of TMS-Cl and subsequent chloride abstraction using Na[X].<sup>30</sup> Heating a fluorobenzene solution containing [1][BArF<sub>24</sub>] and phenylacetylene to 120 °C gave the [2+2] cycloaddition product [2a][BArF<sub>24</sub>] as an off-white, moisture sensitive solid in quantitative yield (Scheme 2). The oxaphosphete salt [2a][BArF<sub>24</sub>] shows a characteristic doublet at -14.6 ppm ( ${}^{2}J_{PH}$  = 17 Hz) in the  ${}^{31}P$  NMR spectrum, which appears at lower frequency than the <sup>31</sup>P NMR signal of the oxophosphonium ion  $[1]^+$  (+59.0 ppm). The formation of the four-membered heterocycle is further confirmed by the <sup>13</sup>C NMR spectrum, revealing a doublet at 99.9 ppm  $(^{1}J_{PC} = 109 \text{ Hz})$  for the phosphorus-bound carbon atom and a doublet at 163.5 ppm ( ${}^{2}J_{PC}$  = 28 Hz) of the adjacent carbon atom which is deshielded by the oxygen atom. The <sup>1</sup>H NMR signal of the ring proton appears at 3.99 ppm and is significantly shifted to lower frequency compared to that of the parent oxete  $C_3H_4O$  (6.70 ppm) $^{52}$  or the metallaoxete Cp\*\_2Ti(OCPhCH) (7.67 ppm). $^{53}$  The effect can be rationalized by an enhanced polarization of the C=C bond of the four-membered ring as a results of the negative hyperconjugation of  $\pi$  electron density from the carbon atom into low lying  $\sigma^*$  orbitals of the phosphorus atom.



Figure 1. Solid-state structure of [2a][OTf]. Only one of the two crystallographically independent molecules is depicted. Hydrogen atoms, the OTf anion and a disordered iPr group are omitted for clarity. Ellipsoids are drawn at 50 % probability. Selected bond lengths [Å] and angles [°]: P–N1 1.557(3), P–N4 1.557(3), P–O 1.677(2), P–C1 1.766(3), C1–C2 1.324(5), C2–O 1.413(4), P-O-C2 88.6(2), N1-P-N4 109.0(2), P-C1-C2 87.9(2), C1-C2-O 105.2(3), O-P-C1 78.3(2).

Single crystals suitable for X-ray diffraction studies were obtained for the triflate salt [**2a**][OTf]. Two crystallographically independent molecules were found with different orientation of the bulky R<sup>1</sup> substituents relative to the oxaphosphete unit leading to minor differences in bond lengths and angles. The molecular structure and selected structural parameters of one oxaphosphete cation  $[2a]^+$  are depicted in Figure 1. The oxaphosphete ring is perfectly planar (sum of angles: 360°) and kite-like distorted, as evident by the small O-P-C1 angle of 78° and rather large C1-C2-O angle of 105°. The C1–C2 bond (1.314 Å) and the C2–O bond (1.413 Å) are in the range of typical C=C double and C-O single bonds, respectively. The P–O bond of 1.677 Å is considerably elongated compared to the similarly substituted phosphine oxide  ${}^{t}Bu({}^{i}PrHN)_{2}PO$  (1.489 Å)<sup>54</sup> and to the acyclic phosphonium salt [Me(Me<sub>2</sub>N)<sub>2</sub>POCH<sub>2</sub><sup>t</sup>Bu][I] (1.546 Å)<sup>55</sup>, which indicates a rather weak P-O bond in  $[2a]^+$ . The cycloaddition reaction between [**1**][OTf] and phenylacetylene is less selective (cf. Figure S9), therefore only the  $[BArF_{24}]^{-}$  anion was used in further studies.

Scheme 2. Synthesis of oxaphosphete salts [2a-f][BArF<sub>24</sub>]. Dipp = 2,6-diisopropylphenyl.

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Table 1. Scope of terminal alkynes in [2+2]cycloaddition reactions with oxophosphonium salt [1][BArF<sub>24</sub>]. <sup>a</sup>Conversion according to <sup>1</sup>H NMR spectroscopy after 40 hours when the reaction was stopped.

Entry compou R conditions yi nd $1  [2b]^+  p-Me_2N-C_6H_4-  r.t., 30 \text{ min } 99$ $2  [2c]^+  p-Me_2N-C_6H_4-  r.t., 30 \text{ min } 99$	
1 $[2b]^+$ p-Me <sub>2</sub> N-C <sub>6</sub> H <sub>4</sub> - r.t., 30 min 99	eld
$2 [2a] + m M_{0} O C I = (0.9 C 2 h) O($	9%
$2 [20]^{-1} p-me0-c_6 n_4 - 60 c, 5 m 95$	9%
3 [ <b>2d</b> ]⁺ <i>p</i> -Me-C <sub>6</sub> H <sub>4</sub> − 100 °C, 12 h 99	9%
4 [ <b>2a</b> ] <sup>+</sup> Ph- 120 °C, 12 h 99	9%
<sup>5</sup> $[2e]^+$ <sup>3,5-(CF<sub>3</sub>)-</sup> <sub>C<sub>6</sub>H<sub>3</sub>- 180 °C, 40 h <sup>35</sup></sub>	5% <sup>a</sup>
6 $[2f]^+$ <i>n</i> Pr- 60 °C, 19 h 79	9%

22 In order to explore possible substituent effects on the 23 [2+2] cycloaddition reaction, a series of sterically and 24 electronically different phenylacetylene derivatives were 25 reacted with oxophosphonium salt [1][BArF<sub>24</sub>] (Scheme 2, 26 Table 1), which gave the oxaphosphete salts [2b-27 d][BArF<sub>24</sub>] in quantitative yield. The cycloaddition reaction 28 with electron rich alkynes is significantly faster than with 29 phenylacetylene, in particularly with a  $\pi$ -donating 30 dimethylamino (Entry 1) or a methoxy group (Entry 2) in 31 para position to the acetylene unit, suggesting a step-wise 32 reaction pathway for these substrates rather than a 33 concerted cycloaddition. By contrast, forcing reaction conditions are required for the cycloaddition reaction with 34 electron deficient alkynes (Entry 5). Heating a 35 fluorobenzene solution of [1][BArF<sub>24</sub>] and 1-Ethynyl-3,5-36 bis(trifluoromethyl)benzene in a sealed NMR tube at 180 37 °C for 40 hours resulted in only 35% conversion to the 38 oxaphosphete salt  $[2e][BArF_{24}]$ . However, the reaction 39 might additionally be hampered by the increased steric 40 bulk of the alkyne compared with the other 41 phenylacetylene derivatives. The cycloaddition reaction 42 between  $[\mathbf{1}][BArF_{24}]$  and 1-pentyne has the same 43 regioselectivity as with aryl alkynes, but is slightly less 44 selective (Entry 6). The internal alkynes tolane and 1-45 phenyl-1-propyne did not undergo cycloaddition reactions 46 with [1][BArF<sub>24</sub>] even at elevated temperature (180 °C) indicating the importance of steric effects in the 47 cycloaddition reaction. 48

49 Collectively, this study reveals that the [2+2] cycloaddition reactions between the heavy main group carbonyl 50 analogue  $[1][BArF_{24}]$  and terminal alkynes afford the 51 corresponding oxaphosphetes [**2a-f**][BArF<sub>24</sub>] with reaction 52 rates that strongly depend on the electronic properties of 53 the respective alkynes. The reaction is regioselective and 54 gives the heterocycle with the phenyl group adjacent to the 55 oxygen atom as the only product. The same regioselectivity 56 was observed for the carbonyl-alkyne metathesis 57

reaction<sup>56,57</sup> and for the cycloaddition reaction between phenylacetylene derivatives and sterically encumbered Ti(IV) oxido complexes.<sup>32,33,38,39</sup> The less bulky Zr(IV) oxido complexes, however, show the inverse regioselectivity,<sup>31,32</sup> indicating the dominance of steric effects, which might also control the selectivity in the case of oxophosphonium ion  $[1]^+$ .

Cycloreversion. Previously, Bergman and Hull demonstrated that oxametallacyclobutenes I undergo alkyne exchange reactions at room temperature illustrating the reversibility of the metal oxido-alkyne cycloaddition reaction.53,58 We found that oxaphosphete ions show a similar behavior, however, the exchange reaction requires harsher reaction conditions. Heating a dichloromethane solution of the heterocycle [2a][BArF<sub>24</sub>] with an equimolar amount of 4-ethynyltoluene in a sealed NMR tube to 120 °C resulted in the slow conversion to the oxaphosphete salt [2d][BArF<sub>24</sub>] (Scheme 3). <sup>1</sup>H and <sup>31</sup>P NMR monitoring of the reaction progress revealed that the maximum conversion of 57% was achieved after three days (Table S1). Interestingly, the characteristic resonance of the free oxophosphonium ion  $[1]^+$  can be detected at 59.1 ppm in the <sup>31</sup>P NMR spectrum of the reaction mixture. The generation of small amounts of  $[1]^+$  during the reaction suggests a sequential alkyne elimination/addition mechanism for the exchange reaction. Similarly, phosphirenium salts undergo dissociative alkyne exchange reactions via transient phosphenium ions.59

## Scheme 3: Reaction of oxaphosphete [2a][BArF<sub>24</sub>] with 4-ethynyltoluene.



To prove this hypothesis, we heated a neat sample of [2a] [BArF<sub>24</sub>] with a heat gun at approximately 300 °C for one minute. This gave the free oxophosphonium salt [1][BArF<sub>24</sub>] and phenylacetylene in 73% yield, as evidenced by NMR spectroscopy and gas chromatography (Scheme 4, top). To further examine the thermal cleavage of  $[2a][BArF_{24}]$ in solution, we used N,N-dimethylaminopyridine (DMAP) to trap the generated free oxophosphonium ion [1]<sup>+</sup> (Scheme 4, bottom). Note that DMAP readily reacts with [1]<sup>+</sup> at room temperature to give the Lewis base adduct [1(DMAP)]<sup>+,30</sup> but it does not react with the oxaphosphete ion  $[2a]^+$  at moderate temperatures. In fact, heating a mixture of [2a][BArF<sub>24</sub>] and DMAP in fluorobenzene at 100 °C for 16 hours gave the Lewis base adduct  $[1(DMAP)]^+$  in less than 5% yield. Complete alkyne elimination and formation of the trapping product [1(DMAP)]<sup>+</sup> required prolonged heating to 150 °C, which is consistent with a high energy barrier for the cycloreversion reaction.

Scheme 4: Thermally induced cycloreversion of





Computational studies. DFT methods<sup>60</sup> at the PW6B95-D3/def2-TZVPP<sup>61-63</sup> level of theory were used to determine the energy profile of the cycloaddition reaction of  $[1]^+$  with phenylacetylene. The energy profile is shown in Error! Reference source not found.. Separated reactants (SR) were taken as reference. The computed structure of the initial reactant complex (RC) shows an approach of the terminal carbon atom of the alkyne to the phosphorus atom with a distance of 2.94 Å. The cycloaddition reaction has a reaction barrier of 12.6 kcal/mol (TS1) and results in the formation of oxaphosphete [2a]⁺ (closed form, CF). CF is thermodynamically favoured over the open form (OF) by 13.7 kcal/mol with an opening barrier of 22.6 kcal/mol (TS2). The calculated energy profile agrees with the experimentally observed stability and isolation of the closed form ([2a]<sup>+</sup>). Nevertheless, the relatively low energy barrier of the ring opening indicates that both open (**OF**) and closed (CF) forms are in equilibrium at higher temperatures.

Using the DLPNO-CCSD(T)/def2-TZVPP<sup>61,62,64-69</sup> method, we next examined the substituent effect in oxophosphonium ions on the energy profile of the cycloaddition reaction and compared the reactivity with that of ketones (Figure 3). As model systems the reaction of phenylacetylene with four different electrophiles was considered: acetone (reaction **b**), an "unstabilized" dimethyloxophosphonium ion (reaction **c**), an oxophosphonium ion bearing N-heterocyclic imines (NHI) as used experimentally (reaction **d**), an oxophosphonium ion comprising one NHI and one N-heterocyclic olefin (NHO) substituent as previously prepared<sup>30</sup> (reaction **e**).

The profile the reaction energy of between phenylacetylene and acetone (**b**) is similar to that of the previously investigated uncatalyzed reactions between formaldehyde and methoxyacetylene<sup>15</sup> or acetaldehyde and acetylene.<sup>70</sup> As expected for the uncatalyzed reaction, the [2+2] cycloaddition reaction has a high activation barrier of 59.3 kcal/mol, which is significantly higher than those of the oxophosphonium ions (c-e). The oxete intermediate (CF-b) is unstable with respect to electrocyclic ring opening via the second transition state  $(\Delta G^{\ddagger} = 25.8 \text{ kcal/mol})$  to afford the  $\alpha$ , $\beta$ -unsaturated ketone (**OF-b**). The high energy first transition state (**TS1**) and the fact that the open form is the thermodynamically stable product are key differences to the energy profiles of the heavier phosphorus congeners (reactions c-e). These differences are particularly evident for the unstabilized oxophosphonium ion  $[Me_2P=0]^+$  (c), which forms the most stable oxaphosphete in this series with a barrier of 36.8 kcal/mol to the open form. Moreover, the alkyne addition constitutes a stepwise process due to the high electrophilicity at phosphorus. Natural Bond Orbital (NBO)<sup>71</sup> analysis confirms that the reactant complex (**RC-c**) is a  $\sigma$ -bonded species which is formed without a barrier. The C···P distance (1.93 Å) is in the range of an elongated C-P single bond and the geometries around the P and C atom are significantly distorted from the previous planar and linear structure, respectively (see Figure S67 for the structure).

By employing  $\pi$ -donor substituents at the phosphorus atom (reactions **e** and **d**), the energy difference between the open and closed form gets smaller compared to the simple model (**c**). Formal replacement of one NHI with a NHO substituent has little influence on the overall reaction



Figure 2. Free energy profile of the cycloaddition reaction of  $[1]^+$  with phenylacetylene (reaction **a**) calculated at PW6B95-D3/def2-TZVPP. Dipp-groups are shown in wireframe and hydrogens are omitted for clarity.

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ΔG

[kcal/mol]

60

40

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-20

-40

0.0

RC

-12.1

19.2

-19 5

-41.1

path. However, it increases the first barrier by 6.8 kcal/mol and reduces the second barrier by 8.1 kcal/mol. As a result, the energy difference between **CF-e** and **OF-e** is only 7.2 kcal/mol with a barrier of 11.0 kcal/mol, suggesting electrocyclic ring-opening and ring-closing even at room temperature. The transition state geometries of **TS2-d** and **TS2-e** are very similar (Figure S79) with P–O bond distances of 2.47 Å (**TS2-d**) and 2.41 Å (**TS2-e**), while the natural population analysis (NPA) gives a significantly larger natural charge on phosphorus for **TS2-d** (2.022) than for **TS2-e** (1.827) (cf. Table S8). Hence, the difference among the transition state energy seems to be governed by electronic effects rather than structural parameters.

TS1

47 2

- E = C, R' = R" = Me

CF

26.0

E = P, R' = R" = Me

R

OF

23.0

23.3

38.5

-45.3

TS2

-0.2

17.5

19.2



-34 9

**Reactivity of the oxaphosphete ion [2a]**<sup>+</sup>. Our computational results indicate that the acyclic 1-phospha-4-oxa-butadiene state of  $[2a]^+$  is thermally accessible, which prompted us to investigate whether it can be trapped by [4+2] hetero Diels-Alder cycloaddition reactions. Similar to  $\alpha,\beta$ -unsaturated carbonyls, which are important dienes in hetero Diels-Alder reactions for material and natural product synthesis,<sup>72</sup> phosphabutadiene derivatives have been used in cycloaddition reactions for the construction of phosphorus-containing heterocycles.<sup>73-81</sup> Furthermore, neutral  $\sigma^3\lambda^5$ -phosphoranes containing the P=C-C=O system were postulated as reactive intermediates based on their ability to undergo [4+2] cycloaddition reactions with polar multiple bonds.<sup>82,83</sup>

52The reaction of the oxaphosphete salt [2a][BArF24] with53acetonitrile and benzaldehyde gave the [4+2]54cycloaddition products [3a][BArF24] and [4][BArF24] as air-55stable solids in quantitative yield, respectively (Scheme 5).56The required high reaction temperature is consistent with57the 22.6 kcal/mol barrier (Figure 2) for the ring opening of58

[2a] [BArF<sub>24</sub>]. NMR spectroscopic studies (Table 2) reveal that the <sup>31</sup>P NMR resonances of the six-membered rings appear at lower frequencies ([**3a**]<sup>+</sup>: -43.3 ppm,  ${}^{2}J_{PH}$  = 3 Hz,  $[4]^+$ : -20.0 ppm,  ${}^2J_{PH} = 11$  Hz,  ${}^3J_{PH} = 12$  Hz) than that of the four-membered heterocycle ([2a]⁺: -14.8 ppm,  $^{2}I_{PH}$  = 18 Hz). The computed  $^{31}P$  NMR resonances of selected model compounds agree with the experimental data and show that the size of the heterocycle has negligible influence on the phosphorus chemical shift (cf. Figure S72, Table S9). As a result of the insertion into the P–O bond, the  ${}^{2}J_{CP}$  coupling to the CO-carbon atoms reveal significantly smaller coupling constants ([4]<sup>+</sup>: 3 Hz) than in [2a]<sup>+</sup> (28 Hz). The ring expansion reaction was confirmed by XRD studies on single crystals of [3a][BArF<sub>24</sub>] grown by layering a saturated acetonitrile solution with *n*-pentane (Figure 4). In the molecular structure, the oxazaphosphininium ring is perfectly planar (sum of angles: 720°) bearing C1-N1 (1.261 Å) and C3-C4 (1.336 Å) bond lengths in the range of double bonds and a tetrahedrally coordinated phosphorus atom.





Table 2: Selected <sup>31</sup>P and <sup>13</sup>C NMR shifts and coupling constants of oxaphosphete cation [2a]<sup>+</sup> and its cycloaddition products [3a]<sup>+</sup>, [4]<sup>+</sup>. <sup>a</sup>Coupling constant is below NMR resolution.

entry	compound	δ ( <sup>31</sup> P) [ <sup>2</sup> J <sub>PH</sub> ]	δ( <sup>13</sup> C , <i>C</i> P) [ <sup>1</sup> J <sub>CP</sub> ]	δ( <sup>13</sup> C, CO) [ <sup>2</sup> J <sub>CP</sub> ]
1	[2a]⁺	-14.8 ppm [18 Hz]	99.9 ppm [109 Hz]	163.5 ppm [28 Hz]
2	[3a]⁺	-43.3 ppm [3 Hz]	95.4 ppm [133 Hz]	157.5 ppm [-]ª
3	<b>[4]</b> <sup>+</sup>	-20.0 ppm [11 Hz]	92.8 ppm [152 Hz]	160.4 ppm [3 Hz]

Remarkably, the formation of  $[3a]^+$  is entirely reversible. Heating of the neat samples with a heat gun at approximately 300 °C for one minute affords the free oxophosphonium  $[1]^+$  ion via two consecutive cycloreversion reactions in 82% yield according to NMR analysis (Scheme 6). The cycloreversion of  $[3a]^+$  was confirmed by a nitrile exchange experiment using 4methoxybenzonitrile (Scheme 6). Prolonged heating resulted in the formation of a mixture of  $[3b]^+$  (62%) and  $[3a]^+$  (26%) in addition to small amounts of  $[2a]^+$  (6%) and  $[1]^+$  (3%). The thermolysis of [4][BArF<sub>24</sub>] is unselective and gives a complex mixture containing  $[2a]^+$  and several other phosphorus species according to the  $^{31}\mathrm{P}$  NMR analysis.

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Scheme 6: Nitrile exchange reaction (top) and thermally induced cycloreversion (bottom). R'CN = p-MeO-C<sub>6</sub>H<sub>4</sub>CN.



The insertion of nitriles into the P–O bonds of oxaphosphirane and oxaphosphetane complexes was recently reported.<sup>47,84</sup> However, unlike oxaphosphetes, the saturated congeners require the acid-induced P–O bond cleavage prior to the nitrile insertion. Beyond main-group elements, ring expansion reactions have been reported for oxazirconacyclobutenes **I**. The insertion of aldehydes occurs selectively into the Zr–C bond rather than the Zr–O bond, resulting in six membered heterocycles with O-Zr-O structural motif.<sup>35,58</sup>



Figure 4 Solid-state structure of [4a][BArF<sub>24</sub>]. Hydrogen atoms (except H3) and the BArF<sub>24</sub> anion are omitted for clarity. Ellipsoids are displayed at 50 % probability. Dipp groups are showed in wireframe for clarity. Only one part of disordered Dipp and phenyl groups is depicted. Average selected bond lengths [Å] and angles [°]: P–N1 1.671(2), P–C3 1.763(2), C3–C4 1.336(3), N1–C1 1.261(3), C1–O 1.375(2), C4–O 1.384(2), N1-P-C3 102.34(9), P-C3-C4 121.6(2), C3-C4-O 123.2(2), C4-O-C1 121.5(2), C1-N1-P 124.0(2).

#### Summary

Oxophosphonium ion  $[1]^+$ , which can be regarded as heavy main group carbonyl analogue, undergoes [2+2] cycloadditions with terminal alkynes to generate the first oxaphosphete cations [**2a-e**]<sup>+</sup>. Alkyne exchange experiments and trapping reactions reveal that the formation of these strained four-membered heterocycles is reversible, while the addition rate strongly depends on the electronic properties of the alkynes. Quantum chemical calculations show that the use of  $\pi$ -donor substituents at the phosphorus atom triggers the electrocyclic ring opening of the oxaphosphete ions to the 1-phospha-4-oxabutadiene structure at elevated temperature. This property of [**2a**]<sup>+</sup> was exploited to generate six-membered heterocycles [**3a**]<sup>+</sup> and [**4**]<sup>+</sup> via [4+2] hetero Diels-Alder reactions with acetonitrile and benzaldehyde, respectively.

Interesting analogies can be recognized with respect to the cycloaddition reactions of oxophosphonium ion [1]<sup>+</sup>, zirconium oxido complex [Cp\*<sub>2</sub>Zr=0] and ketones. Both  $[1]^+$  and  $[Cp_2T=0]$  afford four-membered heterocyclic products in the [2+2] cycloaddition reaction with alkynes. The reactions proceed without a catalyst and are reversible. In the case of carbonyls, however, acyclic  $\alpha$ , $\beta$ unsaturated carbonyl compounds are irreversibly formed and a catalyst is required owing to the high energy barriers associated with the reaction. With respect to the subsequent reactivity of the cycloaddition products, oxaphosphete ion  $[2a]^+$  resembles  $\alpha,\beta$ -unsaturated carbonyls as the analogous 1-phospha-4-oxa-butadiene isomer is formed upon thermal cleavage of the P-O bond and it can be used as diene in hetero Diels-Alder reactions. In contrast, oxazirconacyclobutenes (I) undergo rearrangement reactions at elevated temperature and insertion reactions occur exclusively into the Zr-C bond of the metallacycle. Considering the analogy to the carbonylalkyne metathesis, the cycloaddition reaction between oxophosphonium ions and alkynes is an intriguing example of the diagonal relationship between carbon and phosphorus in the periodic table. Furthermore, the analogy to metal oxido complexes corroborates the notion that ambiphilic main group elements such as the phosphenium fragment  $(R^1)_2 P^+$  in  $[1]^+$  can act as mimics for transition metals.85-87

#### ASSOCIATED CONTENT

The supporting information is available free of charge at <a href="https://pubs.acs.org/">https://pubs.acs.org/</a>

Synthetic procedures, NMR spectra, mass spectrometry data, crystallographic data and computational details.

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529x529mm (96 x 96 DPI)





176x79mm (220 x 220 DPI)



219x241mm (150 x 150 DPI)



82x40mm (299 x 299 DPI)