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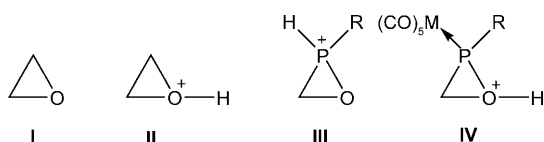
## Protonation of Oxaphosphiranes

## Protonation-Induced Rearrangement of an Oxaphosphirane Complex\*\*

Janaina Marinas Pérez, Holger Helten, Bruno Donnadieu, Christopher A. Reed, and Rainer Streubel\*

Dedicated to Professor Wolf-Walter du Mont on the occasion of his 65th birthday

Epoxides **I** (oxiranes) are important building blocks in organic synthesis, particularly in natural product and polymer chemistry.<sup>[1,2]</sup> Despite numerous experimental<sup>[3–6]</sup> and theoretical investigations,<sup>[7–9]</sup> oxiranium cations **II** have remained especially elusive proposed intermediates of acid-catalyzed ring-opening reactions. By comparison, protonation of  $\sigma^3\lambda^3$ -oxaphosphiranes<sup>[10–14]</sup> would presumably<sup>[15]</sup> yield P-protonated oxaphosphiranium species **III**, which are also unknown. In principle,  $\kappa P$  metal coordination of a  $\sigma^3\lambda^3$ -oxaphosphirane complex should divert protonation to yield oxaphosphiranium complexes **IV**, and kinetic stabilization with a bulky substituent at phosphorus might allow observation of a closed-ring cation.



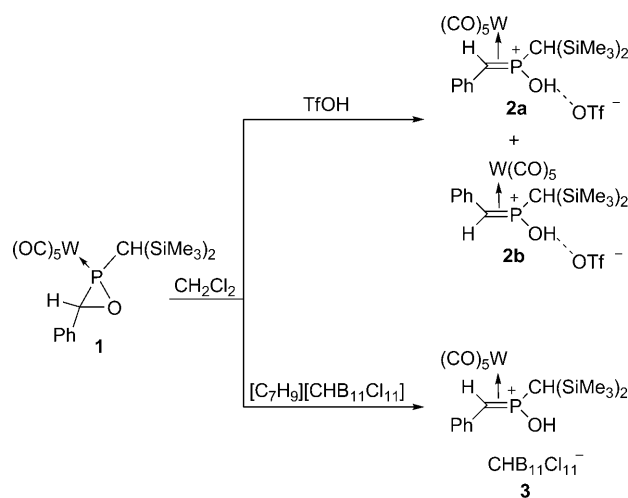
Although oxaphosphirane complexes were first described by Mathey and co-workers almost 20 years ago,<sup>[16]</sup> and new synthetic methods, such as phosphinidene complex transfer to carbonyls<sup>[17,18]</sup> and reaction of phosphinidenoid complexes<sup>[19,20]</sup> with aldehydes,<sup>[19,21]</sup> have since been developed, the chemistry of oxaphosphiranes remains relatively undeveloped. The first designed application was found in the triflic acid induced P–O ring expansion reaction with nitriles.<sup>[22]</sup> We accidentally discovered a thermal C–O bond cleavage reaction that provides access to novel O,P,C cage ligands.<sup>[23]</sup>

As the titanium(III)-induced ring-opening of oxiranes has found numerous synthetic applications,<sup>[24]</sup> the feasibility of C–O and/or P–O bond cleavage of an oxaphosphirane complex by titanium(III) has also recently been investigated theoretically.<sup>[25]</sup>

Herein, we report that the protonation of a coordinated oxaphosphirane leads to a complex bearing a novel side-on-bonded P–C ligand, which can be described as a methylene phosphonium ion; DFT calculations provide information on the low-energy pathway to its formation and the effects of substituents on the process.

The oxaphosphirane complex **1**<sup>[17]</sup> was reacted with triflic acid in dichloromethane to selectively yield complexes **2a,b** in 86:14 ratio (Scheme 1). Product **2a** displayed a <sup>31</sup>P signal at  $\delta = 73.8$  ppm in the NMR spectrum with a very small tungsten–phosphorus coupling constant  $^1J_{W,P} = 113.2$  Hz, indicative of side-on bonding to the metal complex moiety,<sup>[26]</sup> whereas **2b** showed a <sup>31</sup>P signal at  $\delta = 72.3$  ppm with even smaller  $^1J_{W,P}$  coupling (97.9 Hz). Neither <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy nor IR spectroscopy on **2a,b** were particularly informative, and attempts to separate **2a** from **2b** by column chromatography or crystallization failed.

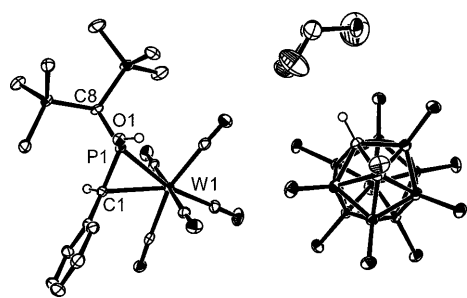
The superior crystallizing properties of carborane anions as counterions for reactive cations<sup>[27]</sup> suggested that X-ray structural information on **2a,b** might be obtained using a carborane acid instead of triflic acid. Thus, reaction of **1** under similar conditions with the toluenium ion salt, [C<sub>7</sub>H<sub>9</sub>]


 Scheme 1. Products from the protonation of the oxaphosphirane complex **1**.

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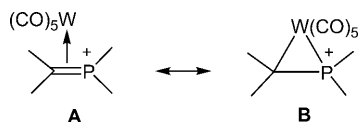
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**Figure 1.** Structure of **3**-CH<sub>2</sub>Cl<sub>2</sub> (ellipsoids set at 50% probability; hydrogen atoms except H1, H2, H3 are omitted for clarity). Selected bond lengths [Å] and angles [°]: W1–P1 2.4513(5), W1–C1 2.4489(17), P1–O1 1.5935(14), P1–C1 1.7394(18); C1–W1–P1 41.58(4), P1–C1–W1 69.28(9), C1–P1–W1 69.14(6).

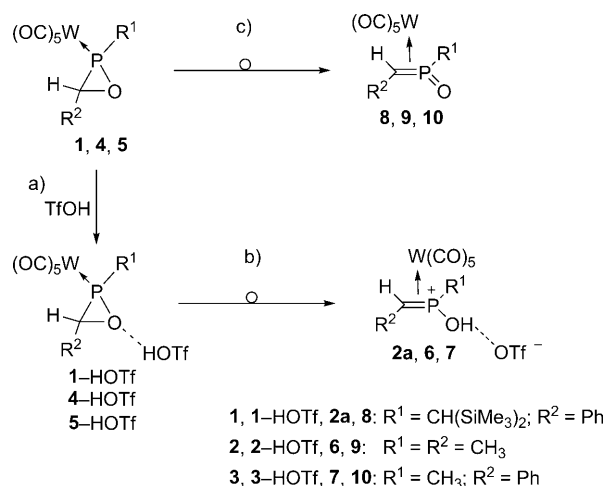
[CHB<sub>11</sub>Cl<sub>11</sub>], a somewhat weaker acid than triflic acid but with a less-basic anion,<sup>[28]</sup> led exclusively to a single product **3** with similar, although not identical, NMR spectroscopic data to **2a,b** ( $\delta(^{31}\text{P}) = 75.5$  ppm,  $^1J_{\text{WP}} = 108.0$  Hz).

The molecular structure<sup>[29]</sup> of **3** reveals a coordinated methylene phosphonium ion that is side-on bonded to the W(CO)<sub>5</sub> group (Figure 1). The P–OH group forms a weak H-bond to Cl6 of the carborane anion (O–H = 1.75 Å, H⋯Cl = 2.51 Å, O⋯Cl = 3.26 Å, and  $\angle$ O–H–Cl = 177°). Comparison of the cationic ligand in **3** with structurally characterized free methylene phosphonium ions [(*i*Pr<sub>2</sub>N)<sub>2</sub>P=C(SiMe<sub>3</sub>)<sub>2</sub>OTf]<sup>[30]</sup> and [(*t*Bu)<sub>2</sub>P=C(Ph)<sub>2</sub>][AlCl<sub>4</sub>]<sup>[31]</sup> shows that the P1–C1 bond in **3** is lengthened approximately 0.1 Å by coordination to tungsten, but is still shorter than a typical P–C single bond. The environments at the P1 and C1 centers deviate from the planarity expected of a side-on coordinated, Z-configured P=C double bond in **A**, which points to a contribution of the structure **B** to the ground state.



The very close similarity of the NMR spectroscopic data for the triflic acid products **2a,b** and the carborane acid product **3** suggests that they all have the same fundamental cationic structure. Given the greater basicity and smaller size of the triflate anion relative to CHB<sub>11</sub>Cl<sub>11</sub><sup>−</sup>, the difference between **2** and **3** probably lies in the ability of triflate to engage in stronger H-bonding with the P–OH group of the cation. Finally, the appearance of isomers **2a** and **2b** is presumably explained in terms of a haptotropic shift via diastereomeric transition states. As the free-energy preference of **2a** over **2b** is only a few kJ mol<sup>−1</sup>, we are cautious about speculating on its precise origin, but the absence of isomers in **3** suggests an explanation must include H-bonding of the triflate anion.

To gain further insight into the mechanism of the reaction of **1** with triflic acid, DFT calculations were performed on two model complexes **4** (R<sup>1</sup> = R<sup>2</sup> = CH<sub>3</sub>) and **5** (R<sup>1</sup> = CH<sub>3</sub>, R<sup>2</sup> = Ph) and on the full system **1** (Scheme 2, reactions a and b).



**Scheme 2.** Computed TfOH-induced ring opening and valence isomerization of complexes **1**, **4**, and **5**.

Furthermore, the valence isomerization of **1**, **4**, and **5** to methyleneoxophosphorane complexes **8**, **9**, and **10** (c) was computed for comparison,<sup>[32]</sup> relative free energies are given in Table 1.

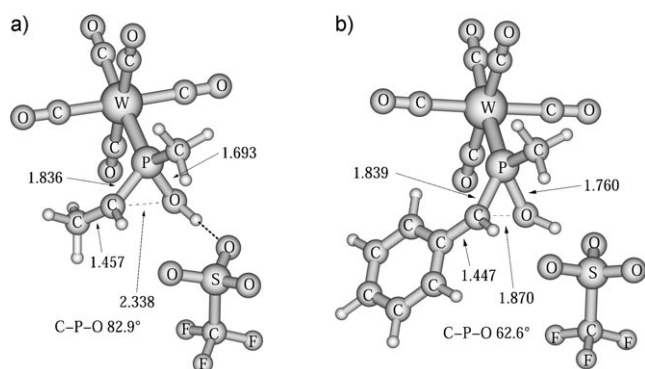
In the first, slightly endergonic step (a), the oxaphosphirane complex and triflic acid form an associate (**1**-HOTf, **4**-HOTf, **5**-HOTf) in which the acid proton is bound to the oxaphosphirane oxygen center by O–H–O hydrogen bonding. Upon proton transfer, C–O ring bond cleavage<sup>[33]</sup> and haptotropic shift of the W(CO)<sub>5</sub> fragment proceed in a concerted manner (b), leading to the exergonic formation of the final products **2a**, **6**, and **7**. This explains why the O-protonated oxaphosphirane complex **1** was not observed, even at −80 °C. The barrier for this process is strongly influenced by the substituent on the carbon atom of the oxaphosphirane, and decreases considerably if a phenyl substituent is present (R<sup>2</sup> at C3). This is also apparent from the transition-state structures (Figure 2). When R<sup>2</sup> = Ph, lengthening of the C–O bond is significantly less pronounced, indicating an earlier transition state; in each case, the TfOH proton is already transferred to the ring oxygen. During cleavage of the C–O bond, the positive charge that is emerging at the C3 center is effectively stabilized by the phenyl group through  $\pi$ -electron conjugation.<sup>[34]</sup>

Valence isomerization (c), without preceding activation by an acid, is almost thermoneutral for the three systems computed, but the barriers are considerably higher than those of reaction (b). Also here, the C-phenyl substituent stabilizes the transition state, whilst the presence of the bulky CH-

**Table 1:** Calculated thermochemical data for reactions shown in Scheme 2 (all values in kJ mol<sup>−1</sup>).<sup>[a]</sup>

Reaction	R <sup>1</sup> = R <sup>2</sup> = CH <sub>3</sub>		R <sup>1</sup> = CH <sub>3</sub> , R <sup>2</sup> = Ph		R <sup>1</sup> = CH(SiMe <sub>3</sub> ) <sub>2</sub> , R <sup>2</sup> = Ph	
	$\Delta G_{298}^{\ddagger}$	$\Delta_R G_{298}$	$\Delta G_{298}^{\ddagger}$	$\Delta_R G_{298}$	$\Delta G_{298}^{\ddagger}$	$\Delta_R G_{298}$
a	– <sup>[b]</sup>	+13.6	– <sup>[b]</sup>	+17.2	– <sup>[b]</sup>	+29.5
b	+75.5	–32.6	+44.8	–43.1	+53.3	–30.2
c	+134.3	+4.4	+96.6	–2.8	+123.6	+14.9

[a] B3LYP/aug-TZVP/ECP-60-MWB(W) COSMO (CH<sub>2</sub>Cl<sub>2</sub>)/RI-BLYP/aug-SV(P)/ECP-60-MWB(W) COSMO (CH<sub>2</sub>Cl<sub>2</sub>). [b] Not calculated.



**Figure 2.** Calculated structures of the transition states of the TfOH-induced ring opening (reaction b in Scheme 2) of two model systems. Bond distances in Å.

(SiMe<sub>3</sub>)<sub>2</sub> group at phosphorus causes a significant increase of the barrier.

## Experimental Section

All the reactions were carried out in an inert atmosphere using purified and dried argon and standard Schlenk techniques in case of complex **2**, and in a glove box (H<sub>2</sub>O, O<sub>2</sub> < 0.5 ppm) for complex **3**. Solvents were dried over sodium wire or CaH<sub>2</sub> (CH<sub>2</sub>Cl<sub>2</sub>) and distilled under argon. NMR data were recorded on a Bruker DMX 300 spectrometer at 30 °C using CDCl<sub>3</sub> and CD<sub>2</sub>Cl<sub>2</sub> as solvent and internal standard; shifts are given relative to tetramethylsilane (<sup>13</sup>C: 75.5 MHz) and 85% H<sub>3</sub>PO<sub>4</sub> (<sup>31</sup>P: 121.5 MHz). IR spectra were recorded by using a Shimadzu-8300 FTIR spectrometer in the  $\tilde{\nu}$  = 4000–450 cm<sup>-1</sup> range.

**2a,b:** Complex **1**<sup>[17]</sup> (40 mg, 0.064 mmol) was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (0.6 mL), and TfOH (7  $\mu$ L, 0.070 mmol) was added at ambient temperature. After 5 minutes the reaction is complete. The solvent was removed under vacuum and the green oil thus obtained (47.5 mg, 92% yield) was dissolved in CDCl<sub>3</sub>. Only the data for the major isomer (ratio 86:14) are given. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 30 °C, TMS):  $\delta$  = 0.20 (s, 9H; Si(CH<sub>3</sub>)<sub>3</sub>), 0.40 (d, 1H, <sup>2</sup>J<sub>PH</sub> = 10.5 Hz; CH(SiMe<sub>3</sub>)<sub>2</sub>), 0.48 (s, 9H; Si(CH<sub>3</sub>)<sub>3</sub>), 3.20 (d, 1H, <sup>2</sup>J<sub>PH</sub> = 16.3 Hz; CHPh), 7.40 ppm (m<sub>c</sub>; 5H, Ph); <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, CDCl<sub>3</sub>, 30 °C, TMS):  $\delta$  = -0.1 (d, <sup>3</sup>J<sub>PC</sub> = 4.2 Hz; Si(CH<sub>3</sub>)<sub>3</sub>), 0.1 (d, <sup>3</sup>J<sub>PC</sub> = 2.9 Hz; Si(CH<sub>3</sub>)<sub>3</sub>), 15.0 (d, <sup>1</sup>J<sub>PC</sub> = 16.5 Hz, PCHPh), 18.1 (d, <sup>1</sup>J<sub>PC</sub> = 24.6 Hz; PCH(Si(CH<sub>3</sub>)<sub>3</sub>)<sub>2</sub>), 117.0 (q, <sup>1</sup>J<sub>FC</sub> = 317.0 Hz; SO<sub>2</sub>CF<sub>3</sub>), 126.5 (d, <sup>3</sup>J<sub>PC</sub> = 2.3 Hz; Ph), 126.8 (s; Ph), 127.6 (s; *p*-Ph), 134.3 (d, <sup>2</sup>J<sub>PC</sub> = 6.1 Hz; *i*-Ph), 190.4 ppm (d, <sup>2</sup>J<sub>PC</sub> = 9.7 Hz; CO); <sup>31</sup>P NMR (121.5 MHz, CDCl<sub>3</sub>, 30 °C, 85% H<sub>3</sub>PO<sub>4</sub>):  $\delta$  = 73.8 ppm (dd<sub>sat</sub>, <sup>1</sup>J<sub>WP</sub> = 113.2 Hz, <sup>2</sup>J<sub>PH</sub> = 16.5 Hz, <sup>2</sup>J<sub>PH</sub> = 10.5 Hz); IR (Nujol):  $\tilde{\nu}$   $\approx$  3500 (very br;  $\nu$ (OH)); this band is even broader than that of pure triflic acid), 2072 (w;  $\nu$ (CO)), 2002 (m;  $\nu$ (CO)), 1980 (s;  $\nu$ (CO)), 1937 (s;  $\nu$ (CO)), 1870 (m;  $\nu$ (CO)), 844 cm<sup>-1</sup> (m; Ph).

**3:** Complex **1** (33 mg, 0.053 mmol) was dissolved in CD<sub>2</sub>Cl<sub>2</sub> (0.6 mL), and [C<sub>7</sub>H<sub>5</sub>][CHB<sub>11</sub>Cl<sub>11</sub>]<sup>[27]</sup> (30 mg, 0.050 mmol) was added at ambient temperature. After 10 minutes the reaction was complete. Colorless crystals of **3** (48.5 mg, 79% yield) were obtained from diffusion-controlled crystallization into the reaction solution using *n*-hexane. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, 30 °C, TMS):  $\delta$  = 0.32 (s, 9H; Si(CH<sub>3</sub>)<sub>3</sub>), 0.50 (s, 9H; Si(CH<sub>3</sub>)<sub>3</sub>), 1.00 (d, 1H, <sup>2</sup>J<sub>PH</sub> = 6.9 Hz; CH(Si(CH<sub>3</sub>)<sub>3</sub>)), 3.40 (d, 1H, <sup>2</sup>J<sub>PH</sub> = 17.4 Hz; CHPh), 3.20 (br, 1H; CHB<sub>11</sub>Cl<sub>11</sub>), 7.4 (m<sub>c</sub>, 3H; Ph), 7.5 ppm (m<sub>c</sub>, 2H; Ph); <sup>13</sup>C{<sup>1</sup>H} NMR (75 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 30 °C, TMS):  $\delta$  = 2.4 (d, <sup>3</sup>J<sub>PC</sub> = 2.7 Hz; Si(CH<sub>3</sub>)<sub>3</sub>), 2.5 (d, <sup>3</sup>J<sub>PC</sub> = 4.7 Hz; Si(CH<sub>3</sub>)<sub>3</sub>), 17.9 (d, <sup>1</sup>J<sub>PC</sub> = 15.9 Hz; PCHPh), 21.0 (d, <sup>1</sup>J<sub>PC</sub> = 21.6 Hz; PCH((Si(CH<sub>3</sub>)<sub>3</sub>)<sub>2</sub>)), 47.1 (s; CHB<sub>11</sub>Cl<sub>11</sub>), 129.0 (d, <sup>1</sup>J<sub>PC</sub> = 8.9 Hz; Ph), 129.2 (d, <sup>1</sup>J<sub>PC</sub> = 3.5 Hz; Ph), 130.5 (s; *p*-Ph), 136.1 (s; *i*-Ph), 193 ppm (d, <sup>2</sup>J<sub>PC</sub> = 9.6 Hz, CO); <sup>31</sup>P NMR (121.5 MHz, CD<sub>2</sub>Cl<sub>2</sub>,

30 °C, 85% H<sub>3</sub>PO<sub>4</sub>):  $\delta$  = 75.5 ppm (dd<sub>sat</sub>, <sup>1</sup>J<sub>WP</sub> = 118.0 Hz, <sup>2</sup>J<sub>PH</sub> = 17.1 Hz, <sup>2</sup>J<sub>PH</sub> = 11.5 Hz); IR (Nujol):  $\tilde{\nu}$  = 3387 (br;  $\nu$ (OH)), 2117 (w;  $\nu$ (CO)), 2067 (m;  $\nu$ (CO)), 2037 (s;  $\nu$ (CO)), 2023 (s;  $\nu$ (CO)), 1992 (m;  $\nu$ (CO)), 831 cm<sup>-1</sup> (m; Ph).

DFT calculations were carried out with the TURBOMOLE V5.8 program package.<sup>[36a]</sup> For optimizations,<sup>[36b]</sup> the gradient-corrected exchange functional by Becke<sup>[37]</sup> (B88) in combination with the gradient-corrected correlation functional by Lee, Yang, and Parr<sup>[38]</sup> (LYP) with the RI approximation<sup>[39]</sup> and the valence-double- $\zeta$  basis set SV(P)<sup>[40]</sup> was used. For the oxaphosphirane oxygen and the O atoms belonging to triflate (or triflic acid), the basis was augmented with uncontracted gaussian functions having an exponent of 0.0845 (one of each type), and the sulfur basis set was augmented with diffuse basis functions having exponents of 0.0405. For tungsten, the effective core potential ECP-60-MWB<sup>[41]</sup> was employed. The influence of the polar solvent was taken into account by employing the COSMO approach<sup>[42]</sup> with  $\epsilon$  = 8.93. For cavity construction, the atomic radii of Bondi,<sup>[43]</sup> obtained from crystallographic data, were used; the atomic radius of tungsten was set to 2.2230 Å. Transition states were located by using a TRIM algorithm.<sup>[44]</sup> Excellent initial guesses were obtained through relaxed surface scans along the major reaction coordinates. All stationary points were characterized by numerical vibrational frequency calculations.<sup>[45]</sup> Single-point calculations were carried out using the three-parameter hybrid functional Becke3<sup>[46]</sup> (B3) in combination with the correlation functional LYP<sup>[38]</sup> using the valence-triple- $\zeta$  basis set TZVP<sup>[47]</sup> which was augmented as specified above, and ECP-60-MWB<sup>[41]</sup> for tungsten. The COSMO approach<sup>[42]</sup> was employed with the same parameters as used for optimizations. Zero-point corrections and thermal corrections to free energies were adopted from frequencies calculations on the optimization level (RI-BLYP/aug-SV(P)/ECP-60-MWB(W) + COSMO). It has been shown that this approach is appropriate for reactions of epoxide, aziridine, and thiirane with methanethiolate.<sup>[48]</sup> Atomic charges were calculated based on shared electron numbers (SENs).<sup>[49]</sup>

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**Keywords:** epoxides · haptotropic shifts · oxaphosphiranes · protonation · tungsten

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- [34] In the transition state, the CHPh fragment holds a positive charge of +0.62 au, of which the major part is delocalized over the phenyl group (+0.52 au). The C3 center is coordinated in a trigonal planar manner (torsion angle P-C3-H-Cl<sub>phenyl</sub> 178.5°), and the phenyl ring adopts an almost co-planar arrangement with the plane given by P-C3-H. The C3-Cl<sub>phenyl</sub> bond is shortened by about 3% with respect to the reactant. In the further course of the pathway, the electron deficiency at the CHPh fragment is canceled by formation of the P–C double bond ( $q(\text{CHPh}) = 0.00$  au in complex **7**).
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