Title
Protonation-induced rearrangement of an oxaphosphirane complex

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Epoxides I (oxiranes) are important building blocks in organic synthesis, particularly in natural product and polymer chemistry.[1,2] Despite numerous experimental[3–6] and theoretical investigations,[7–9] oxiranium cations II have remained especially elusive proposed intermediates of acid-catalyzed ring-opening reactions. By comparison, protonation of \( \text{O}_3\text{P}_3\)oxaphosphiranes[10–14] would presumably[15] yield P-protonated oxaphosphiranium species III, which are also unknown. In principle, \( \kappa^P \) metal coordination of a \( \text{O}_3\text{P}_3\)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,[16] and new synthetic methods, such as phosphinidene complex transfer to carbonyls[17,18] and reaction of phosphinideno complexes[19,20] with aldehydes,[19,21] have since been developed, the chemistry of oxaphosphiranes remains relatively undeveloped. The first designed application was found in the triflic acid induced P/O\(_2\) ring expansion reaction with nitriles.[22] We accidentally discovered a thermal C/O\(_2\) bond cleavage reaction that provides access to novel O,P,C cage ligands.[23,24] As the titanium(III)-induced ring-opening of oxiranes has found numerous synthetic applications,[24] the feasibility of C–O and/or P–O bond cleavage of an oxaphosphirane complex by titanium(III) has also recently been investigated theoretically.[25]

Herein, we report that the protonation of a coordinated oxaphosphirane leads to a complex bearing a novel side-on-bonded P/C\(_2\)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[17] was reacted with triflic acid in dichloromethane to selectively yield complexes 2a, 2b in 86:14 ratio (Scheme 1). Product 2a displayed a \( ^{31}\text{P} \) signal at \( \delta = 73.8 \text{ ppm} \) in the NMR spectrum with a very small tungsten–phosphorus coupling constant \( J_{\text{W,P}} = 113.2 \text{ Hz} \), indicative of side-on bonding to the metal complex moiety,[26] whereas 2b showed a \( ^{31}\text{P} \) signal at \( \delta = 72.3 \text{ ppm} \) with even smaller \( J_{\text{W,P}} \) coupling (97.9 Hz). Neither \( ^1\text{H} \) and \( ^{13}\text{C} \) NMR spectroscopy nor IR spectroscopy on 2a, 2b were particularly informative, and attempts to separate 2a from 2b by column chromatography or crystallization failed.

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[CHB(CH)2Cl]4, a somewhat weaker acid than triflic acid but with a less-basic anion,† led exclusively to a single product 3 with similar, although not identical, NMR spectroscopic data to 2a,b (δ(P)=75.5 ppm, JPP=108.0 Hz).

The molecular structure[20] of 3 reveals a coordinated methylene phosphonium ion that is side-on bonded to the W(CO)5 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 O–H–Cl=177°). Comparison of the cationic ligand in 3 with structurally characterized free methylene phosphonium ions in [(PPh3)2P=C(SiMe3)2]OTf[26] and [(Bu)2P=C(Ph)2][AlCl4][31] shows that the P1–Cl1 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-configurated P–C double bond in A, which points to a contribution of the structure B to the ground state.

![Figure 1. Structure of 3-CH2Cl4 (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–Cl1=2.4489(17), P1–O1 1.5935(14), P1–Cl1=1.7394(18); C1–W1–P1 41.58(4), P1–C1–W1 69.28(9), C1–P1–W1 69.14(6).](Image 86x676 to 257x782)

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 CHB11Cl11, the difference between 2 and 3 probably lies in the ability of triflate to OH group forms a weak H-bonding with the P/C0-OH group of the transition state, whilst the presence of the bulky CH-

Furthermore, the valence isomerization of 1, 4, and 5 to methyleneoxophosphorane complexes 8, 9, and 10 (c) was computed for comparison,[32] 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[33] and haptotropic shift of the W(CO)5 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 (R2 at C3). This is also apparent from the transition-state structures (Figure 2). When R2=Ph, lengthening of the C–O bond is significantly less pronounced, indicating an earlier transition state; in each case, the TIOH 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 π-electron conjugation.[34]

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-

![Scheme 2. Computed TIOH-induced ring opening and valence isomerization of complexes 1, 4, and 5.](Image 313x604 to 534x782)

![Table 1: Calculated thermochemical data for reactions shown in Scheme 2 (all values in kJ mol−1).][a]![Table 1: Calculated thermochemical data for reactions shown in Scheme 2 (all values in kJ mol−1).][a]

<table>
<thead>
<tr>
<th>Reaction</th>
<th>R2′=CH3</th>
<th>R2′=Ph</th>
<th>R2′=CH(SiMe3)2</th>
</tr>
</thead>
<tbody>
<tr>
<td>ΔG298+</td>
<td>ΔG298+</td>
<td>ΔG298+</td>
<td>ΔG298+</td>
</tr>
<tr>
<td>a</td>
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<td>+17.2</td>
<td>+29.5</td>
</tr>
<tr>
<td>b</td>
<td>+3.26</td>
<td>+4.84</td>
<td>+33.3</td>
</tr>
<tr>
<td>c</td>
<td>+134.3</td>
<td>+96.6</td>
<td>+123.6 +14.9</td>
</tr>
</tbody>
</table>

According to the discussion on the effect of phosphorus on the SiMe3 group mentioned in the text, the (SiMe3)2 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 an a glove box (H2O, O2 < 0.5 ppm) for complex 3. Solvents were dried over sodium wire or CaH2 (CH2Cl2) and distilled at ambient temperature. After 10 minutes the reaction was complete. The solvent was removed under vacuum and the green oil thus obtained (47.5 mg, 92% yield) was dissolved in CDCl3. Only the data for the major isomer (ratio 86:14) are given. 1H NMR (300 MHz, CDCl3, 30°) 6.1 Hz; Si(CH3)3), 0.40 (d, 1H, JPC = 4.7 Hz; Si(CH3)3), 2.9 Hz; Si(C(CH3)3), 0.1 (d, JPC = 2.9 Hz; Si(CH3)3), 15.0 (d, JPC = 16.5 Hz, PCHPh), 18.1 (d, JPC = 24.6 Hz; PCH(Si(CH3)3)), 177.0 (q, JPC = 31.0 Hz; SO2CH3), 126.5 (d, JPC = 2.3 Hz; Ph), 126.8 (s; Ph), 127.6 (s; Ph), 134.3 (d, JPC = 6.1 Hz; i-Ph), 190.4 ppm (d, JPC = 9.7 Hz; CO); 31P NMR (121.5 MHz, CDCl3, 30°, 85% H3PO4): JPC = 113.2 Hz, JPP = 16.5 Hz, JPO = 10.5 Hz; IR (Nujol): f ≈ 3500 (very br; v(OH); this band is even broader than that of pure triflic acid), 2072 (w; v(CO)). 2002 (m; v(CO)), 1980 (s; v(CO)), 1937 (s; v(CO)), 1870 (m; v(CO)), 844 cm–1 (m; Ph).

Complex 3 (53 mg, 0.053 mmol) was dissolved in CDCl3 (0.6 mL), and [CH2Br2C]2[Cl]31 (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. 1H NMR (300 MHz, CDCl3, 30°, TMS): δ = 0.32 (s, 9H; Si(CH3)3), 0.50 (s, 9H; Si(CH3)3), 1.00 (d, 1H, JPP = 6.9 Hz; CH2Si(CH3)3), 3.40 (d, 1H, JPP = 17.4 Hz; CH2P), 3.20 (br, 1H; CH3Br), 7.4 (m, 3H1); 7.5 ppm (m, 2H1); 31P NMR (121.5 MHz, CDCl3, 30°, TMS): δ = 2.4 (d, JPP = 2.7 Hz; Si(CH3)3), 2.5 (d, JPC = 4.7 Hz; Si(CH3)3), 17.9 (d, JPC = 15.9 Hz; PCHPh), 21.0 (d, JPC = 21.6 Hz; PCH(Si(CH3)3)), 47.1 (s; CH2Br,Cl), 129.0 (d, JPC = 8.9 Hz; Ph), 129.2 (d, JPC = 3.5 Hz; Ph), 130.5 (s; p-Ph), 136.1 (s; i-Ph), 193 ppm (d, JPC = 9.6 Hz, CO); 13C NMR (121.5 MHz, CDCl3, 30°, 85% H3PO4): δ = 75.5 ppm (dd, JCH = 118.0 Hz, JPC = 17.1 Hz, JPC = 11.5 Hz); IR (Nujol): f = 3387 (br; v(OH)), 2117 (w; v(CO)), 2067 (m; v(CO)), 2037 (s; v(CO)), 2023 (s; v(CO)), 1992 (m; v(CO)), 831 cm–1 (m; Ph).

IR frequencies were carried out with the TURBOMOLE V5.8 program package. For optimizations the gradient- corrected exchange functional by Becke [88] in combination with the gradient-corrected correlation functional by Lee, Yang, and Parr [89] (LYP) with the RI approximation [90] and the valence-double-ζ basis set 6-31G(2d,p) [91] was used. For phospholene 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 [92] was employed. The influence of the polar solvent was taken into account by employing the COSMO approach [93] with ε = 8.93. For cavity construction, the atomic radii of Bondi [94] 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 [95]. Excellent initial guesses were obtained through relaxed surface scans along the major reaction coordinates. All stationary points were characterized by numerical vibrational frequency calculations [46]. Single-point calculations were carried out using the three-parameter hybrid functional Becke3 [96] (B3) in combination with the correlation functional LYP [97] using the valence-triple-ζ basis set TZVP [98] which was augmented as specified above, and ECP-60-MWB [92] for tungsten. The COSMO approach [99] 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 thirane with methanethiolate [100]. Atomic charges were calculated based on shared electron numbers (SENs) [101].

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For calculations that reveal complex III with R = CH₃ is favored over its OH tautomer by 6.6 kJ mol⁻¹ (B3LYP/aug-TZVP/ECP-60-MWB(W) COSMO (CH₂Cl₂)/RI-BLYP/aug-SV(P)/ECP-60-MWB(W) COSMO (CH₂Cl₂)).


Crystal structure determination for 3: C₃H₅B₆Cl₂O₂PSiW, M = 1228.20, triclinic, space group P1 (no. 2), a = 9.5558(12), b = 14.2372(17), c = 17.852(2) A, α = 86.1740(10), β = 86.5200(10), γ = 70.7550(10°), V = 2285.85(5) A³, Z = 2, T = 123 K, 9875 measured reflections. A crystal 0.51 × 0.12 mm was used to register 10829 intensities (Mo Kα radiation, 2θmax 58.38) on a Bruker APEX-II CCD diffractometer. The structure was solved by Patterson methods (SHELXS-97) and refined (full-matrix least-squares refinement program SHELXL-97) to wR = 0.0430 (for all data), R = 0.0184 (I > 2σ(I)) for 538 parameters and 10829 independent reflections. CCDC 756058 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

For calculations on the valence isomerization of non-coordinated oxaphosphiranes, see: W. W. Schoeller in Multiple Bonds and Low Coordination in Phosphorus Chemistry (Eds.: M. Regitz, O. J. Scherer), Thieme, Stuttgart, 1990, p. 1.

It should be noted that an alternative reaction pathway of 5-HO-TPL the cleavage of the P–O bond, has a slightly lower barrier, which however does not lead to a stable product in the absence of other reagents, such as nitriles (see Ref. [23]).

In the further course of the pathway, the electron deficiency at the phenyl ring (+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-Hphenyl 178.5°), and the phenyl ring adopts an almost co-planar arrangement with the plane given by P-C3-H. The C3-Cphenyl bond is shortened by about 3% with respect to the reactant. In the further course of the pathway, the electron deficiency at the CHPf 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 phenyl 178.5°).


