

## Stable Dioxaphosphirane Species: Facile Formation by Reaction of 10-P-4<sup>1</sup> Hypervalent Phosphoranide with Atmospheric Oxygen

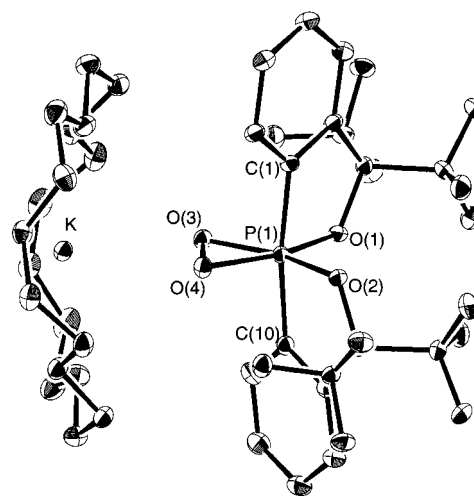
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Dioxaphosphirane, a novel species of P–O–O three membered ring, has been suggested as an intermediate for singlet oxygen oxidation of trivalent phosphorus<sup>2–4</sup> and for decomposition of phosphite ozonide<sup>5</sup> and bisphosphinic peroxides.<sup>6</sup> However, it has never been experimentally established with certainty thus far.<sup>7</sup> Here we report the first isolation and structure of dioxaphosphirane species, 12-P-6 phosphate **5** bearing two Martin ligands and a novel three-membered ring.

When 10-P-4 phosphoranide **2a**,<sup>8,9</sup> potassium 3,3,3',3'-tetrakis(trifluoromethyl)-1,1'-spirobi[3H,2,1λ<sup>5</sup>-benzoxaphosphoranide], [<sup>31</sup>P(THF) δ + 32], was generated from P–H phosphoranide **1a** [<sup>31</sup>P(CDCl<sub>3</sub>) δ –45.8]<sup>9</sup> with KH in THF in the presence of 18-crown-6 and subsequently exposed to the air with stirring at 0 °C, a novel compound **5a** (50%) was found to form and crystallized out of the reaction mixture upon cooling, while 10-P-5 oxidophosphorane **6a** (ca. 30%) remained in the solution (Scheme 1). <sup>1</sup>H, <sup>13</sup>C, and <sup>19</sup>F NMR showed spectra in agreement with a compound of C<sub>2</sub> or C<sub>s</sub> symmetric structure that essentially did not change upon lowering the NMR temperature, and the <sup>31</sup>P NMR signal of δ –121 was indicative of a hexacoordinate 12-P-6 compound **5a**.<sup>10</sup> The aromatic proton (δ 7.75, dd, *J* = 7.46, 14.16 Hz, 2H) ortho to the phosphorus atom was found moderately shifted downfield, suggestive of the presence of polarized bonds, i.e., O–P–O bonds.<sup>11,12</sup> Any presence of ring-opened form 10-P-5 peroxido-phosphoranes could not be observed by NMR. Furthermore,



**Figure 1.** ORTEP Drawing of **5a** without hydrogen atoms for clarity. Selected distances (Å) and angles (deg) for **5a**: P(1)–O(1), 1.745(1); P(1)–O(2), 1.736(1); P(1)–C(1), 1.841(2); P(1)–C(10), 1.850(2); P(1)–O(3), 1.693(1); P(1)–O(4), 1.691(1); O(3)–O(4), 1.560(2); C(1)–P(1)–C(10), 171.8(1); O(3)–P(1)–O(4), 54.9(1); P(1)–O(4)–O(3), 62.6(1); P(1)–O(3)–O(4), 62.5(1); O(1)–P(1)–O(2), 101.5(1); O(1)–P(1)–O(3), 101.7(1); O(2)–P(1)–O(4), 101.9(1); O(1)–P(1)–O(4), 156.5(1); O(2)–P(1)–O(3), 156.8(1).

spin polarization by <sup>19</sup>F NMR showed no sign of exchange between the two pairs of CF<sub>3</sub> groups, thus implying that the compound is quite rigid.<sup>13</sup>

Out of three possible structures of **5a**, **5a'**, and **5a''**, **5a** is most probable but it is rather difficult to determine the structure based on NMR (Scheme 2). X-ray crystallographic analysis determined the structure to be **5a**. Compound **5a** is hexacoordinate bearing a novel three-membered P(O)<sub>2</sub> ring as shown in Figure 1.<sup>14</sup> The molecule possesses approximate C<sub>2</sub> symmetry with the two aromatic carbon substituents trans and four oxygen atoms in the same plane. This indicates that stereochemical change occurred in the phosphoranide moiety from the original configuration in which the two oxygen atoms were disposed trans in the pseudoapical bond. The O–O bond length in **5a** (1.560(2) Å) is almost the same as those for previously reported dioxiranes [Mes<sub>2</sub>C(O<sub>2</sub>): 1.503 Å;<sup>15a</sup> F<sub>2</sub>C(O<sub>2</sub>): 1.578 Å<sup>15b</sup>].

Since the formation of **5a** still occurred upon screening the reaction from light and also in the presence of a <sup>1</sup>O<sub>2</sub> quencher, the reacting O<sub>2</sub> species is the ground state <sup>3</sup>O<sub>2</sub> and not <sup>1</sup>O<sub>2</sub>. Thus, the mechanism of the formation can be formulated as a stepwise process as in Scheme 1. Single-electron transfer (SET) from the phosphoranide **2a** to molecular oxygen generates a reactive pair **3a** of phosphoranyl radical and superoxide anion in cage. Immediate bond formation between the two gives rise to peroxi-

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(7) In a matrix isolation IR study of the decomposition of a phosphine ozonide, a species has been assigned as dioxaphosphirane.<sup>5</sup>

(8) (a) Granoth, I.; Martin, J. C. *J. Am. Chem. Soc.* **1979**, *101*, 4618–4622 and 4623–4626. (b) Chopra, S. K.; Martin, J. C. *Heteroat. Chem.* **1991**, *2*, 71–79. (c) Moon, C. D.; Chopra, S. K.; Martin, J. C. In *Phosphorus Chemistry*; Walsh, E. N., Griffith, E. J., Parry, R. W., Quin, L. D., Eds.; ACS Symposium Series 486; American Chemical Society: Washington, DC, 1992; Chapter 10.

(9) (a) Kojima, S.; Kajiyama, K.; Akiba, K.-y. *Tetrahedron Lett.* **1994**, *35*, 7037–7040. (b) Kojima, S.; Kajiyama, K.; Akiba, K.-y. *Bull. Chem. Soc. Jpn.* **1995**, *68*, 1785–1797. (c) Kojima, S.; Nakamoto, M.; Kajiyama, K.; Akiba, K.-y. *Tetrahedron Lett.* **1995**, *36*, 2261–2264.

(10) **5a**: > 100 °C dec; <sup>1</sup>H NMR(CD<sub>3</sub>CN) δ 3.58 (s, 24H), 7.37 (dd, *J* = 7.16, 7.61 Hz, 2H), 7.45 (dd, *J* = 7.31, 5.94 Hz, 2H), 7.48 (bs, 2H), 7.75 (dd, *J* = 7.46, 14.16 Hz, 2H); <sup>13</sup>C NMR (CD<sub>3</sub>CN) δ 70.9, 124.4 (*J*<sub>CF</sub> = 288 Hz), 124.7 (*J*<sub>CF</sub> = 285 Hz), 128.5 (*J*<sub>PC</sub> = 16.3 Hz), 128.4, 128.7 (*J*<sub>PC</sub> = 25.6 Hz), 130.7 (*J*<sub>PC</sub> = 17.3 Hz); <sup>19</sup>F NMR (CD<sub>3</sub>CN) δ –74.73 (q, *J*<sub>FF</sub> = 8.8 Hz, 6F), –75.36 (q, *J*<sub>FF</sub> = 8.8 Hz, 6F); <sup>31</sup>P NMR (CD<sub>3</sub>CN) δ –121; Anal. Calcd for C<sub>30</sub>H<sub>32</sub>F<sub>12</sub>KO<sub>12</sub>P: C, 42.36; H, 3.79. Found: C, 42.54; H, 3.94.

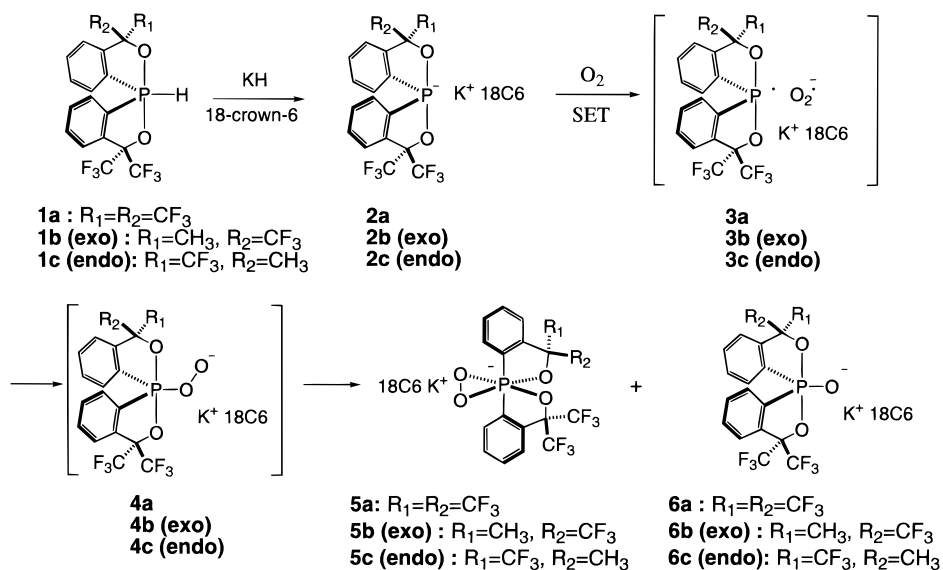
(11) For hexacoordinate compounds of group 16 bearing two Martin ligands, see: (a) Michalak, R. S.; Martin, J. C. *J. Am. Chem. Soc.* **1982**, *104*, 1683–1692. (b) Michalak, R. S.; Wilson, S. R.; Martin, J. C. *J. Am. Chem. Soc.* **1984**, *106*, 7529–7539.

(12) For hexacoordinate compounds of group 15 bearing two Martin ligands see: (a) Yamamoto, Y.; Ohdoi, K.; Chen, X.; Kitano, M.; Akiba, K.-y. *Organometallics* **1993**, *12*, 3297–3303. (b) Kojima, S.; Takagi, R.; Nakata, H.; Yamamoto, Y.; Akiba, K.-y. *Chem. Lett.* **1995**, 857–858. (c) Kojima, S.; Akiba, K.-y. *Tetrahedron Lett.* **1996**, *37*, 8409–8412.

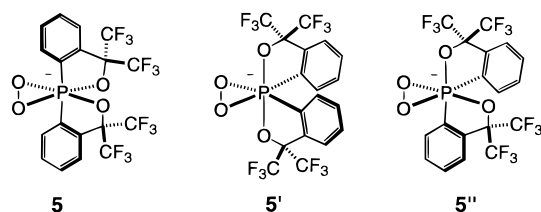
(13) Topological stereochemistry by ring-opening of the three-membered ring followed by ring-closure anti to the opposite oxygen is possible. However, such a transformation does not result in any superficial change in spectra with our symmetric compound. **5a** ⇌ [ring-opened peroxido-phosphorane] ⇌ **5'a**.

(14) The crystal data of **5a**: C<sub>30</sub>H<sub>32</sub>F<sub>12</sub>K<sub>1</sub>O<sub>10</sub>P<sub>1</sub>, molecular weight = 850.63, triclinic, space group *P*-1(No. 2), *a* = 10.446(5) Å, *b* = 12.265(6) Å, *c* = 15.206(6) Å, α = 70.088(3)°, β = 80.669(4)°, γ = 69.164(3)°, *V* = 1710.1(2) Å<sup>3</sup>, *Z* = 2, Mo Kα(λ = 0.71073 Å), 6244 unique reflections measured; 5647 reflections with *I* > 3σ(*I*) used in refinement. *R* = 0.047, *R*<sub>w</sub> = 0.154(a) Sander, W.; Schroeder, K.; Muthusamy, S.; Kirschfeld, A.; Kappert, W.; Boese, R.; Kraka, E.; Sosa, C.; Cremer, D. *J. Am. Chem. Soc.* **1997**, *119*, 7265–7270. (b) Casper, B.; Christen, D.; Mack, H.-G.; Oberhammer, H. Arguello, G. A.; Julicher, B.; Kronberg, M. Willner, H. *J. Phys. Chem.* **1996**, *100*, 3983–3988.

## Scheme 1



## Scheme 2



dioxaphosphorane **4a**. The fluxional nature of trigonal bipyramidal compounds<sup>16</sup> allows **4a** to pseudorotate, ultimately giving a phosphate **5a**. To obtain further insight on the mechanism of dioxaphosphirane formation, diastereomeric analogues were prepared. Phosphoramide **2b (exo)** prepared from phosphorane **1b (exo)** (dr > 99:1) gave rise to the corresponding phosphates **5b (exo)** (dr 97:3; 35%) and **2c (endo)** prepared from **1c<sup>9c</sup> (endo)** (dr 1:>99) formed **5c (endo)** (dr 1:>99; 83%), respectively, with complete retention of relative stereochemistry.<sup>17</sup> This shows that there is not any ring-opening of Martin ligand during the reaction.

(16) (a) Berry, R. S. *J. Chem. Phys.* **1960**, *32*, 933. (b) Holmes, R. R. *Pentacoordinated Phosphorus-Structure and Spectroscopy*; ACS Monograph 175; American Chemical Society: Washington, DC, 1980; Vol. I.

(17) **5b (exo)**: 148 °C dec; <sup>1</sup>H NMR (CD<sub>3</sub>CN) δ 1.55 (s, 3H), 3.52 (s, 24H), 7.37 (dd, *J* = 7.16, 7.61 Hz, 2H), 7.45 (dd, *J* = 7.31, 5.94 Hz, 2H), 7.48 (bs, 2H), 7.75 (dd, *J* = 7.46, 14.16 Hz, 2H); <sup>19</sup>F NMR (CD<sub>3</sub>CN) δ -74.56 (qq, <sup>4</sup>*J*<sub>FF</sub> = 9.3, <sup>7</sup>*J*<sub>FF</sub> = 5.0 Hz, 3F), -75.31 (q, <sup>4</sup>*J*<sub>FF</sub> = 9.3 Hz, 3F), -78.66 (q, <sup>7</sup>*J*<sub>FF</sub> = 5.0 Hz, 3F); <sup>31</sup>P NMR (CD<sub>3</sub>CN) δ -123.2. **5c (endo)**: 161 °C dec; <sup>1</sup>H NMR (CD<sub>3</sub>CN) δ 1.37 (s, 3H), 3.53 (s, 24H), 7.21-7.29 (m, 4H), 7.35 (m, 1H), 7.42 (bs, 1H), 7.55-7.70 (m, 2H); <sup>19</sup>F NMR (CD<sub>3</sub>CN) δ -74.14 (q, <sup>4</sup>*J*<sub>FF</sub> = 9.3 Hz, 3F), -75.41 (q, <sup>4</sup>*J*<sub>FF</sub> = 9.3 Hz, 3F), -79.55 (s, 3F); <sup>31</sup>P NMR (CD<sub>3</sub>CN) δ -123.3.

The interconversion between **5b (exo)** and **5c (endo)** could not be observed in solution (CH<sub>3</sub>CN) during a period of a few days in an ambient environment, thus verifying the stereochemical rigidity of the dioxaphosphiranes. Phosphate **5a** was found to be quite stable in the solid state to ordinary room light as well as to the air at ambient temperature for several months.

Here it should be understood why phosphate **5a** could be isolated, because it is expected that **5a** oxidizes **2a** quickly in solution. Actually, **5a** itself is unexpectedly stable toward **2a** at room temperature, that is, a ca. 1:1 mixture of **5a** and **2a** (0.1 M each in CD<sub>3</sub>CN) lead to less than half conversion to **6a** over 12 h. On the other hand, **5a** reacted instantaneously at ambient temperature with Ph<sub>3</sub>P to give Ph<sub>3</sub>P=O and oxidophosphorane **6a** quantitatively in acetonitrile.<sup>18</sup> The difference is probably due to steric hindrance and it is a lucky reason for the successful isolation of **5** bearing a dioxaphosphirane ring. Further study is being continued.

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**Supporting Information Available:** Detailed crystallographic data for **5a** (PDF). An X-ray crystallographic file, in CIF format, for **5**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(18) **6a**: mp 135 °C; <sup>1</sup>H NMR (CD<sub>3</sub>CN) δ 7.55-7.62 (m, 6H), 8.40 (m, 2H); <sup>19</sup>F NMR (CD<sub>3</sub>CN) δ -74.42 (q, <sup>4</sup>*J*<sub>FF</sub> = 8.8 Hz, 6F), -74.55 (q, <sup>4</sup>*J*<sub>FF</sub> = 8.8 Hz, 6F); <sup>31</sup>P NMR (CD<sub>3</sub>CN) δ -16.5.