Heteroatom Chemistry
Volume 12, Number 4, 2001

# Formation and X-Ray Crystallographic Analysis of a 1,2$\lambda^5$-Oxaphosphol-5(2*H*)-one

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*Received December 18, 2000; revised 16 January 2001*

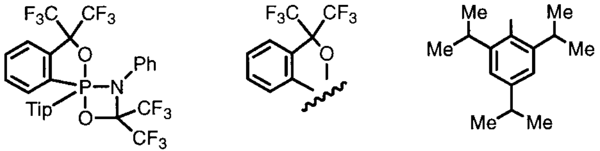
ABSTRACT: *Reaction of an iminophosphorane* **2** *bearing the Martin ligand with dimethyl acetylenedicarboxylate, followed by a ring opening reaction of a [2 + 2]-cycloadduct between them, gave the corresponding α-iminoalkylidenephosphorane* **3***, which was hydrolyzed to afford 1,2*$\lambda^5$*-oxaphosphol-5(2H)-one* **4***. The structure of the novel five-membered ring compound* **4** *was established by X-ray crystallographic analysis*. © 2001 John Wiley & Sons, Inc. Heteroatom Chem 12:282–286, 2001

## INTRODUCTION

There is much interest in the chemistry of iminophosphoranes regarding their characteristic structures in connection with phosphonium ylides [1] and their reactivities, such as aza-Wittig reactions, which are effective methods for the synthesis of nitrogen-containing heterocycles [2]. The reaction of an iminophosphorane with a reactive alkyne has also been studied intensely since it gives the corresponding α-iminoalkylidenephosphorane via a [2 + 2]-cycloadduct between them [3]. In the course of our study on the reactions of an iminophosphorane bearing the Martin ligand [4], we reported the isolation of 1,2$\lambda^5$-azaphosphetidine **1**, that is, the intermediate of the aza-Wittig reaction of the iminophosphorane and hexafluoroacetone (Scheme 1) [5]. Furthermore, using the iminophosphorane and active alkyne, we have found a novel cyclization reaction that provides a new heterocycle that contains a pentacoordinate phosphorus atom. Here, we report the formation and crystal structure of a 1,2$\lambda^5$-oxaphosphol-5(2*H*)-one bearing the Martin ligand and a bulky 2,4,6-triisopropylphenyl (Tip) group.

## RESULTS AND DISCUSSION

Iminophosphorane **2** was generated in situ by the treatment of phenyl azide with a cyclic phosphite which was prepared from $PCl_3$, TipLi, and a dilithio derivative of hexafluorocumyl alcohol as we previously reported (Scheme 2) [5]. Since **2** is sensitive to moisture, it was used as such for the following reactions without further purification. Iminophosphorane **2** in $C_6D_6$ was allowed to react with an excess amount of dimethyl acetylenedicarboxylate (DMAD) at 50°C in a degassed and sealed tube. The monitoring of the above reaction by $^{31}$P NMR spec-



**1** the Martin ligand Tip

**SCHEME 1**

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Dedicated to Professor Naoki Inamoto on the occasion of his 72nd birthday.

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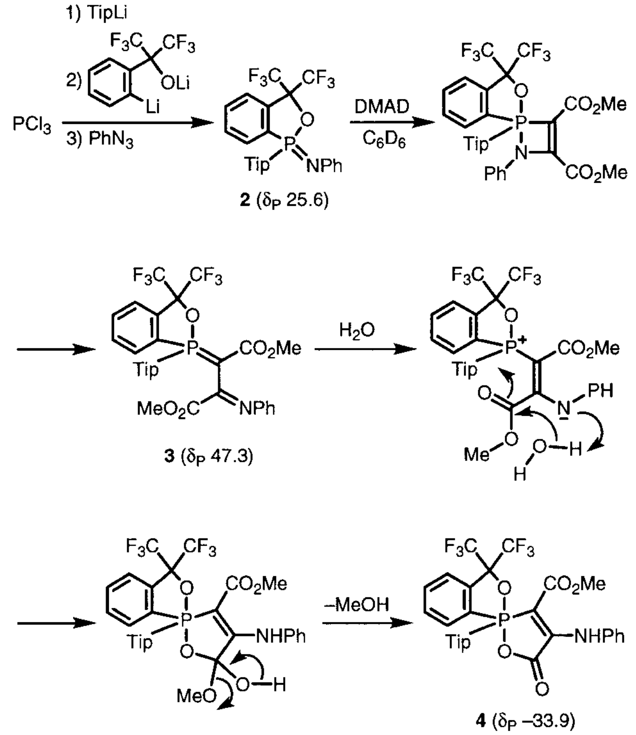
Contract Grant Sponsor: Grants-in-Aid for Scientific Research, Ministry of Education, Science, Sports, and Culture of Japan.



**SCHEME 2**

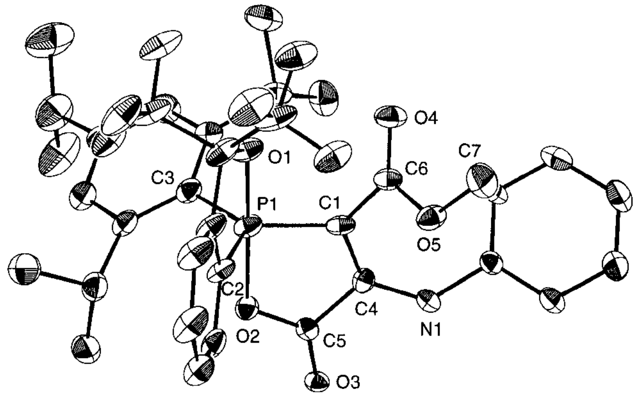


**FIGURE 1** ORTEP drawing of **4** (30% probability). Hydrogen atoms and a solvent molecule are omitted for clarity.

**TABLE 1** Selected Bond Lengths (Å) and Angles (°) of **4**

| | | | |
|---|---|---|---|
| P(1)–O(1) | 1.720(5) | P(1)–O(2) | 1.826(5) |
| P(1)–C(1) | 1.793(7) | P(1)–C(2) | 1.815(7) |
| P(1)–C(3) | 1.837(8) | C(1)–C(4) | 1.365(8) |
| C(1)–C(6) | 1.474(10) | C(4)–C(5) | 1.487(9) |
| C(5)–O(2) | 1.306(7) | C(5)–O(3) | 1.220(7) |
| C(6)–O(4) | 1.207(8) | C(6)–O(5) | 1.336(8) |
| N(1)–C(4) | 1.363(7) | | |
| C(1)–P(1)–C(2) | 113.0(3) | C(1)–P(1)–C(3) | 121.8(3) |
| C(2)–P(1)–C(3) | 125.0(3) | O(1)–P(1)–O(2) | 178.2(2) |
| O(1)–P(1)–C(1) | 94.0(3) | O(1)–P(1)–C(2) | 87.7(3) |
| O(1)–P(1)–C(3) | 92.6(3) | O(2)–P(1)–C(1) | 87.4(3) |
| O(2)–P(1)–C(2) | 90.7(3) | O(2)–P(1)–C(3) | 87.7(3) |
| P(1)–C(1)–C(4) | 112.4(6) | P(1)–C(1)–C(6) | 123.6(5) |
| P(1)–O(2)–C(5) | 115.6(5) | O(2)–C(5)–O(3) | 125.2(7) |
| O(2)–C(5)–C(4) | 110.7(6) | O(4)–C(6)–C(1) | 127.2(7) |
| C(1)–C(4)–C(5) | 113.8(6) | C(4)–C(1)–C(6) | 122.9(7) |
| N(1)–C(4)–C(1) | 132.1(7) | N(1)–C(4)–C(5) | 114.0(6) |

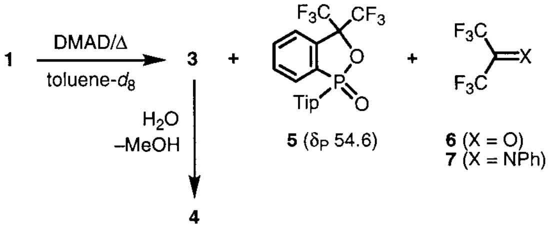
troscopy showed an increase of a new peak ($\delta_P$ 47.3 in $C_6D_6$) with decrease of **2** ($\delta_P$ 25.6), which completely disappeared after heating for 24 hours. The signal assigned to an intermediary [2 + 2]-cycloadduct was not observed. The new compound **3** ($\delta_P$ 47.3) is thermally stable but reactive toward moisture. On exposure to the open air, **3** was slowly converted to the new compound **4**. In the $^1$H NMR spectrum of **4**, the ortho proton of the Martin ligand resonated at low field ($\delta$ 8.32), which is a typical feature of compounds with a trigonal-bipyramidal (TBP) structure bearing a polar apical bond [5,6]. An upfield shift (from $\delta_P$ 47.3 for **3** to $\delta_P$ $-33.9$ for **4** in $C_6D_6$) in the $^{31}$P NMR spectra indicates that **4** has a pentacoordinate phosphorane structure [7].

X-ray crystallographic analysis of **4** finally revealed its TBP structure at the phosphorus atom with two oxygen atoms at the apical positions and three carbon atoms at the equatorial positions as shown in Figure 1. Selected bond lengths and angles are listed in Table 1. The crystal contains molecules of hexane, which exhibits in disordered form. The sum of all C–P1–C angles around the phosphorus atom [359.8(9)°] indicates that the phosphorus atom is placed on the equatorial plane. The bond angle between two apical bonds [178.2(2)°] is comparable to the linearity. The P1–O2 bond length [1.826(5) Å] is apparently longer than the covalent bond radii of P and O atoms [1.76 Å] as in the cases of other apical P–O bonds of phosphoranes exhibiting the TBP geometry [7]. On the other hand, the P1–O1 bond length [1.720(5) Å] is shorter than these values. These phenomena result from the balance of the electronegativity of O1 (alkoxy group) and O2 (carboxy group) [8]. P1–C1, C1–C4, C4–C5, and C5–O2 bond lengths, which are contained in the 1,2-oxaphosphole ring, are in good agreement with the sum of the corresponding covalent bond radii, respectively, taking into consideration the standard deviations. Its 1,2-oxaphosphole ring exists in almost planar form, judging from the torsion angle of P1–C1–C4–C5 and O2–P1–C1–C4 [0.8(7)° and 1.8(4)°, respectively], and the sum of the interior angles of the 1,2-oxaphosphole ring [539.9°]. One conjugated system of an $\alpha,\beta$-unsaturated ketone [C1–C4–C5–O3] is located on the same plane; however, the other [C4–C1–C6–O4] is not, judging from the torsion angles of

C1–C4–C5–O3 and C4–C1–C6–O4 [179.5(5)° and 128.4(8)°, respectively].

The formation of **4** should be most likely explained as follows. The reaction of iminophosphorane **2** with DMAD firstly afforded the corresponding $\alpha$-iminoalkylidenephosphorane **3** via a [2 + 2]-cycloadduct between them similar to the cases of other iminophosphoranes [3]. The formation of **3** was supported by the downfield shift from **2** ($\delta_P$ 25.6) to **3** ($\delta_P$ 47.3) in the $^{31}$P NMR spectra [3a]. On exposure to the open air, the anilide anion that can be depicted as a canonical structure of **3** acts as an intramolecular general base catalyst to assist an attack of oxygen of water on the carbonyl carbon. Subsequent nucleophilic attack of the resulting oxide anion on the phosphorus, followed by elimination of methanol, gives the final product **4** (Scheme 2). There has been only one report on the X-ray crystallographic analysis of a compound with a 1,2$\lambda^5$-oxaphosphol-5(2*H*)-one framework though it is condensed with benzene ring [9]. Although there has been a report on the formation of 1,2$\lambda^5$-oxaphosphol-5(2*H*)-one by the reactions of alkyl diphenylphosphinites with dialkyl acetylenedicarboxylates in the presence of carbon dioxide [10], there has been no report via such a cyclization process. Extremely high electrophilicity of the phosphorus atom promoted by the Martin ligand is most probably considered as a driving force for this novel cyclization process.

Since we have revealed that thermolysis of 1,3,2-oxazaphosphetidine **1** affords iminophosphorane **2** and hexafluoroacetone (denoted as HFA hereafter) [5], we next tried the thermolysis of **1** in the presence of DMAD. The thermolysis of **1** with DMAD in toluene-$d_8$ at 140°C also gave the corresponding ylide **3** (3%) together with cyclic phosphinic ester **5** (56%), HFA **6** (trace), and hexafluoroisopropylideneaniline **7** (41%) (Scheme 3) [11]. On exposure to the open air, **3** was converted to **4** as expected. The formation of **3** and **4** strongly supports the formation of **2** by the thermolysis of **1**.



**SCHEME 3**

In summary, we have shown that reaction of an iminophosphorane **2** bearing the Martin ligand with dimethyl acetylenedicarboxylate gave the $\alpha$-iminoalkylidenephosphorane **3**, which was hydrolyzed to afford 1,2$\lambda^5$-oxaphosphol-5(2*H*)-one **4**. X-ray crystallographic analysis of **4** revealed the planar structure of the novel five-membered ring. The formation of **3** and **4** by the thermolysis of **1** in the presence of DMAD strongly supports the formation of **2**.

## *EXPERIMENTAL*

All reactions were performed under an argon atmosphere unless otherwise noted. Solvents were dried by standard methods and freshly distilled prior to use. Preparative gel permeation liquid chromatography (GPLC) was performed by LC-908 with JAIGEL 1H and 2H columns (Japan Analytical Industry) with toluene as solvent. Preparative thin-layer chromatography (PTLC) was carried out with Merck Kieselgel 60 PF254. The melting point was determined on a Yanaco micro melting point apparatus and was uncorrected. $^1$H (500 MHz) and $^{13}$C (126 MHz) NMR spectra were recorded on a JEOL A500 spectrometer using tetramethylsilane as an internal standard. $^{19}$F (254 MHz) and $^{31}$P (109 MHz) NMR spectra were recorded on a JEOL EXcalibur270 spectrometer using Fleon and 85% $H_3PO_4$ as external standards, respectively. Mass spectral data was recorded on a JEOL SX-102 mass spectrometer. Elemental analysis was carried out at the Microanalytical Laboratory of Department of Chemistry, Faculty of Science, The University of Tokyo.

### *Synthesis of Iminophosphorane* 2

To an ether solution (20 mL) of $PCl_3$ (3.4 mL, 39 mmol) at −70°C was added TipLi, which was prepared from TipBr (4.50 mL, 17.8 mmol) and *n*-BuLi (1.65 M in hexane, 12.0 mL, 19.8 mmol) in ether (18 mL). Then the reaction mixture was warmed to room temperature, and the solvent was evaporated under reduced pressure. The crude material was dissolved in hexane and filtered through Celite. Removal of the solvent gave a yellow solid. To the crude solid were added hexane (75 mL) and $LiC_6H_4C(CF_3)_2OLi$, which was prepared from hexafluorocumyl alcohol (1.50 mL, 8.9 mmol), *n*-BuLi (1.65 M in hexane, 12.0 mL, 19.8 mmol), and TMEDA (0.36 mL, 2.3 mmol) in tetrahydrofuran (THF) (1.5 mL) [4], at −78°C. After having been stirred for 4 hours the reaction mixture was filtered through Celite and evaporated in vacuo to give the crude oil. To the crude oil was added hexane (15 mL) and phenyl azide (0.90 mL, 8.1 mmol) at −78°C. The reaction mixture was warmed to room temperature and evaporated in vacuo to afford a brown oil of the mixture of iminophosphorane **2** and various unidentified products. Iminophosphorane **2** was used for the following reaction without further purification. The formation of **2** was confirmed by $^{19}$F and $^{31}$P NMR spectra. **2**: $^{19}$F NMR ($C_6D_6$, 254 MHz) $\delta$ $-74.41$ (q, $^4J_{FF}$ = 9.1 Hz, 3F), $-75.01$ (q, $^4J_{FF}$ = 9.1 Hz, 3F); $^{31}$P NMR ($C_6D_6$, 109 MHz) $\delta$ 25.6 (s).

### *Reaction of Iminophosphorane* 2 *with Dimethyl Acetylenedicarboxylate*

To a mixture of iminophosphorane **2** (ca. 95 mg) in $C_6D_6$ (0.5 mL) was added dimethyl acetylenedicarboxylate (DMAD) (70 $\mu$L, 0.57 mmol). The amount of **2** was estimated as 0.013 mmol by comparison of the integral in the $^1$H NMR spectra with that of DMAD. The reaction mixture was warmed at 50°C for 24 hours in a degassed and sealed glass tube. The monitoring of the aforementioned reaction solution by $^{19}$F and $^{31}$P NMR spectroscopy showed the disappearance of **2** and the formation of a new peak assigned to $\alpha$-iminoalkylidenephosphorane **3**. After exposure to the open air and removal of the solvent, the reaction mixture was purified with GPLC and PTLC to afford **4** (5.0 mg, 55%). **3**: $^{19}$F NMR (254 MHz, $C_6D_6$) $\delta$ $-74.17$ (q, $^4J_{FF}$ = 9.4 Hz, 3F), $-74.50$ (q, $^4J_{FF}$ = 9.4 Hz, 3F); $^{31}$P NMR (109 MHz, $C_6D_6$) $\delta$ 47.3 (s). **4**: colorless crystals; m.p. 108–112°C (dec.); $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 0.53 (d, $^3J_{HH}$ = 6.7 Hz, 3H), 1.21 (d, $^3J_{HH}$ = 6.9 Hz, 3H), 1.27 (d, $^3J_{HH}$ = 6.3 Hz, 3H), 1.32 (d, $^3J_{HH}$ = 6.7 Hz, 3H), 1.39 (d, $^3J_{HH}$ = 6.3 Hz, 3H), 2.83 (sept, $^3J_{HH}$ = 6.9 Hz, 1H), 2.89 (s, 1H), 3.40 (sept, $^3J_{HH}$ = 6.7 Hz, 1H), 4.73 (sept, $^3J_{HH}$ = 6.3 Hz, 1H), 6.90 (d, $^3J_{HH}$ = 6.9 Hz, 1H), 7.10 (m, 3H), 7.21 (m, 1H), 7.35 (m, 2H), 7.68 (m, 3H), 7.74 (s, 1H, N-*H*), 8.32 (m, 1H); $^{13}$C{$^1$H} NMR (126 MHz, $CDCl_3$) $\delta$ 23.0 (s), 23.59 (s), 23.63 (s), 23.8 (s), 25.2 (s), 25.7 (s), 31.1 (d, $^3J_{CP}$ = 6 Hz), 31.4 (d, $^3J_{CP}$ = 8 Hz), 33.9 (s), 51.3 (s), 82.6 (sept, $^2J_{CP}$ = 31 Hz), 98.3 (d, $^1J_{CP}$ = 172 Hz, P-*C*=C), 121.8 (q, $^1J_{CP}$ = 217 Hz), 121.9 (q, $^1J_{CP}$ = 217 Hz), 122.9 (d, $J_{CP}$ = 17 Hz), 123.2 (s), 123.3 (d, $J_{CP}$ = 17 Hz), 125.2 (d, $J_{CP}$ = 16 Hz), 126.5 (s), 129.3 (s), 131.9 (d, $J_{CP}$ = 14 Hz), 132.9 (d, $^1J_{CP}$ = 151 Hz), 133.0 (d, $^1J_{CP}$ = 186 Hz), 133.6 (d, $J_{CP}$ = 3 Hz), 134.3 (d, $J_{CP}$ = 10 Hz), 136.8 (d, $J_{CP}$ = 22 Hz), 137.6 (s), 146.9 (d, $J_{CP}$ = 28 Hz, P-C=*C*), 149.5 (d, $J_{CP}$ = 15 Hz), 150.0 (d, $J_{CP}$ = 15 Hz), 150.2 (d, $J_{CP}$ = 3 Hz), 163.0 (d, $J_{CP}$ = 3 Hz, P–O–*C*O), 164.2 (d, $J_{CP}$ = 17 Hz, *C*$O_2CH_3$); $^{19}$F NMR (254 MHz, $CDCl_3$) $\delta$ $-74.43$ (q, $^4J_{FF}$ = 9.9 Hz, 3F), $-75.32$ (q, $^4J_{FF}$ = 9.9 Hz, 3F); $^{31}$P NMR (109 MHz) $\delta$ $-37.4$ (s) ($CDCl_3$), $-33.9$ (s) ($C_6D_6$); FABMS: *m/z* 696 ([M + H$^+$]); Anal. Calcd for $C_{35}H_{36}F_6NO_5P$: C, 60.43; H, 5.21; N, 2.01. Found: C, 60.54; H, 5.34; N, 1.93.

### *Thermolysis of 1,3,2-Oxazaphosphetidine* 1 *in the Presence of Dimethyl Acetylenedicarboxylate*

A mixture of **1** (98 mg, 0.13 mmol) and DMAD (0.10 mL, 0.81 mmol) in toluene-$d_8$ (0.6 mL) was heated at 140°C for 25 hours in a degassed and sealed tube. After exposure to the open air and removal of the solvent, the reaction mixture was purified with PTLC to afford **4** (3.5 mg, 5%).

### *X-Ray Data Collection of Compound* 4

Single crystal of **4**-hexane was obtained by the slow evaporation of its saturated solution in hexane at 0°C. The intensity data was collected on a MAC Science DIP-2030 image plate area detector with graphite monochromated Mo K$\alpha$ radiation ($\lambda$ = 0.71069 Å) at 120 K. The structure was solved by direct methods and refined by the full matrix least-squares procedures on $F^2$ (SHELXL-97 [12]). All nonhydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. The final cycle of the least-squares refinement was based on 8020 observed reflections and 529 variable parameters. Crystal data for **4**-hexane: $C_{41}H_{50}F_6NO_5P$, tetragonal, space group $I4_1/a$, $a$ = 34.135(4) Å, $b$ = 14.680(3) Å, $V$ = 17105(4) Å$^3$, $Z$ = 16, $D_c$ = 1.214 g cm$^{-3}$, $R1$ = 0.1127[$I > 2.00\sigma(I)$], w$R2$ = 0.2803 (all data).

### *ACKNOWLEDGMENTS*

We thank Central Glass and Tosoh Finechem Corporation for the gifts of organofluorine compounds and alkyllithiums, respectively.

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