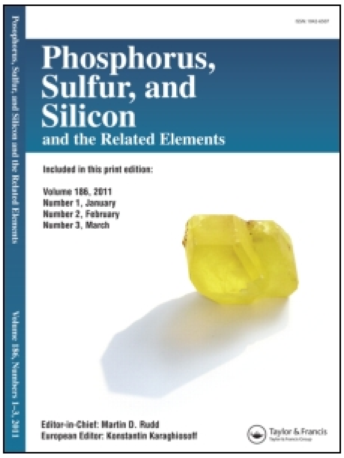


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# SYNTHESIS AND THERMOLYSIS OF PENTACOORDINATE 1,2-AZAPHOSPHETIDINES

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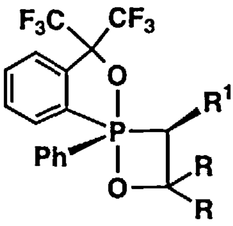
Abstract Pentacoordinate 1,2-azaphosphetidines bearing the Martin ligand were synthesized by the intramolecular dehydration of the corresponding β-amino phosphine oxides with Mitsunobu reagent ($Ph_3P$-$EtO_2CN{=}NCO_2Et$). The X-ray crystallographic analysis of 1,2,4,4,-tetraphenyl derivative shows that it has a distorted trigonal bipyramidal structure with oxygen and nitrogen atoms at apical positions. Their thermolyses gave the corresponding olefins along with a cyclic iminophosphorane, which was readily hydrolyzed to give the cyclic phosphinate and aniline.

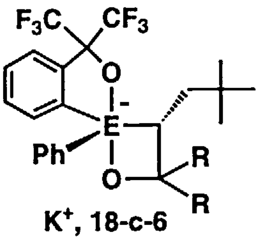


## INTRODUCTION

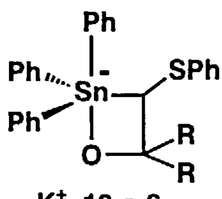
In the course of our study on oxetanes bearing a highly coordinate main group element at the neighboring position we achieved the syntheses and isolation of intermediates of pentacoordinate 1,2-oxaphosphetanes **1a,b**,[1] 1,2-oxasiletanides **2**,[2] 1,2-oxa-germetanides **3**,[3] and 1,2-oxastannetanides **4**,[4] i.e., intermediates of the Wittig, Peterson, germanium-Peterson, and tin-Peterson reactions, respectively. Bestmann and Seng reported phosphorus ylides undergo the Wittig-type reaction with alkylideneamines instead of carbonyl compounds to give the corresponding olefins,[5] but there has been reported no evidence for the intermediates. We now report synthesis and thermolysis of pentacoordinate 1,2-azaphosphetidines which is formally derived from a phosphorus ylide and alkylideneamine.




**1a**: R= H
**1b**: R= $CO_2Me$



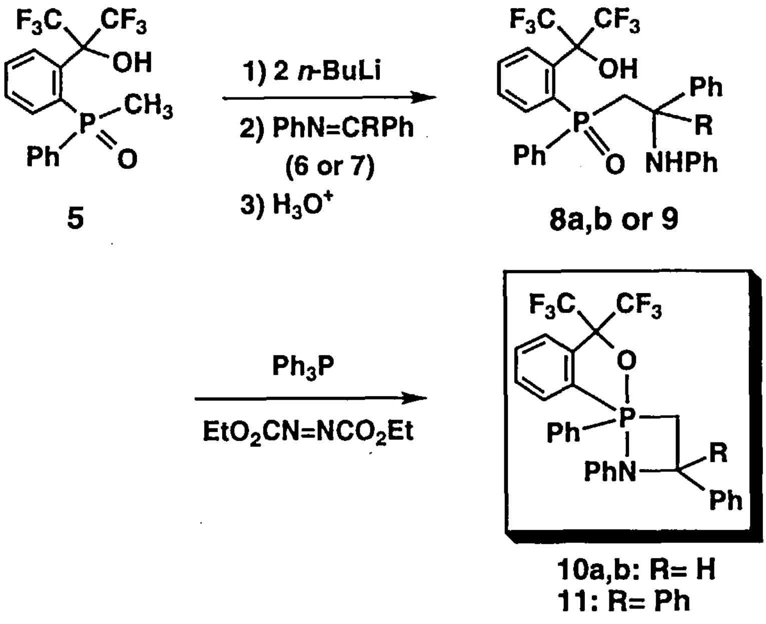

**2**: E= Si
**3**: E= Ge




**4**

## RESULTS AND DISCUSSION

Sequential treatment of methylphenylphosphine oxide (**5**) having the Martin ligand[6] with 2.3 equiv of *n*-BuLi, with 2.4 equiv of benzylideneaniline (**6**) or diphenylmethyleneaniline (**7**) in THF at 0 °C, and then with aqueous $NH_4Cl$ gave a diastereomeric mixture of β-amino phosphine oxides **8a,b** (52%) and **9** (44%) respectively. Intramolecular dehydration of **8a,b** and **9** with Mitsunobu reagent[7] provided target molecules **10a,b** and **11**, respectively. Their $^1$H, $^{19}$F, and $^{31}$P NMR spectral data are partially summarized in Table 1, indicating that **10a,b** and **11** have a trigonal bipyramidal structure with nitrogen and oxygen atoms at apical positions. Compounds **10a,b** were very moisture-sensitive and readily hydrolyzed to the starting **8a,b**, but **11** could be isolated as colorless crystals (73%) by reprecipitation from $CH_2Cl_2$ by the addition of ethanol, indicating that 4,4-diphenyl groups can protect sterically and efficiently the lone pair of the nitrogen atom.



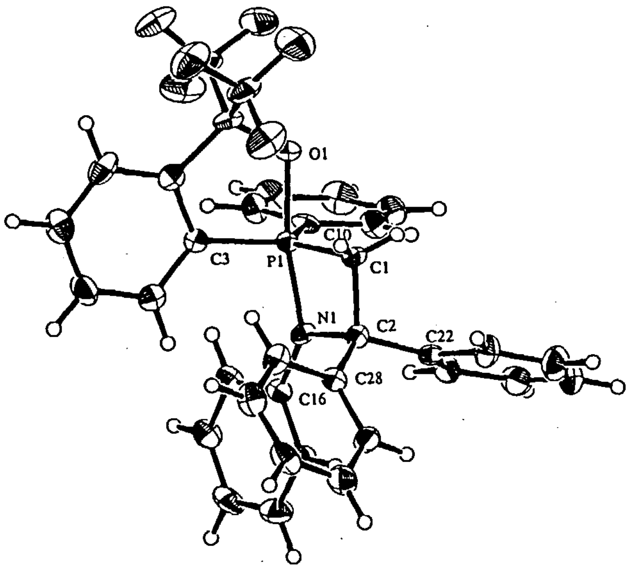

The X-ray crystallographic analysis of **11** indicates that it has a distorted trigonal bipyramidal structure with nitrogen and oxygen atoms at apical positions, very similar to those of pentacoordinate 1,2-oxaphosphetanes **1a,b**, 1,2-oxasiletanides **2**, and 1,2-oxagermetanides **3** (Figure 1). The apical bond P-N (1.789(5) Å) is close to that (1.782(3) Å) of spiro-1,3,2-diazaphosphetidine **12**,[8] but the P-O (1.796(5) Å) bond is slightly longer than those of **1a,b**.[1] The bond angle between two apical bonds deviates by 13.1(3)° from 180°. The phosphorus atom is placed in the equatorial plane and the torsion angle P-C-C-N is -0.1°, indicating that the four membered ring is almost planar. Interestingly, the nitrogen is trigonal and the plane of the benzene ring on the nitrogen is placed in the same plane of the four membered ring.

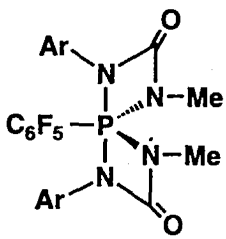
Table 1. The $^{1}H$, $^{19}F$ and $^{31}P$ NMR Data of **10a,b** and **11**.

| | $\delta(^{1}H)$ | | | $\delta(^{19}F)$ | $\delta(^{31}P)$ |
|---|---|---|---|---|---|
| Compounds | CHH' | | CHN | | |
| **10a** | 3.49-3.55(m) | 3.57-3.61(m) | 4.57(m) | -73.5, -74.9$^{a)}$ | -30.6 |
| **10b** | 3.32(ddd)$^{b)}$ | 4.10(ddd)$^{c)}$ | 4.52(ddd)$^{d)}$ | -72.8, -75.2$^{a)}$ | -30.2 |
| **11** | 4.22(dd)$^{e)}$ | 4.55(dd)$^{f)}$ | - | -73.6, -75.5$^{g)}$ | -29.4 |

a) $A_3B_3$ like, not resolved. b) $^{2}J$(HP)= 21.1 Hz, $^{2}J$=16.5 Hz, $^{3}J$=5.0 Hz. c) $^{2}J$(HP)= 19.6 Hz, $^{2}J$=16.5 Hz, $^{3}J$=8.7 Hz. d) $^{3}J$(HP)= 12.2 Hz, $^{3}J$=8.7 Hz, $^{3}J$=5.0 Hz. e) $^{2}J$(HP)= 19.6 Hz, $^{2}J$=17.0 Hz. f) $^{2}J$(HP)= 21.6 Hz, $^{2}J$=17.0 Hz. g) q, $^{4}J$(FF)=9.9 Hz.





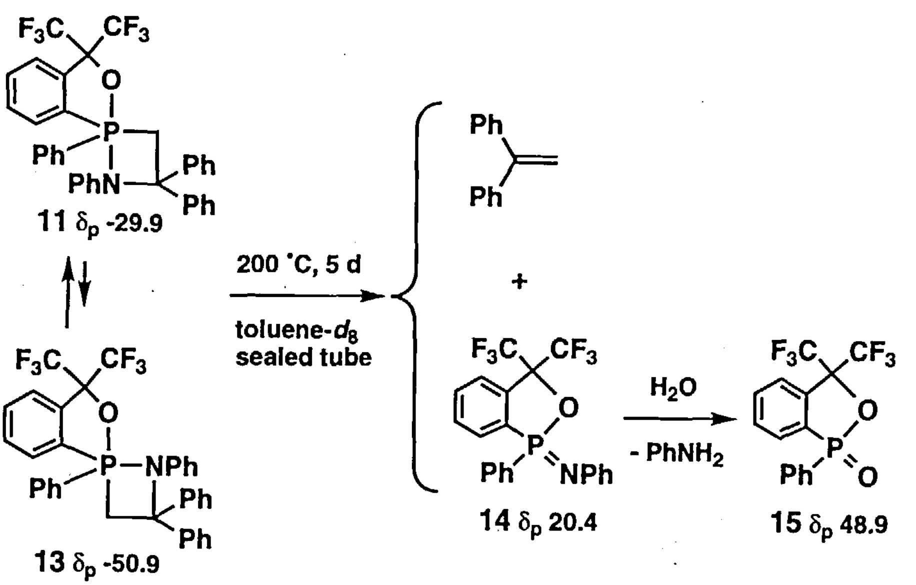



Ar= $m$-$CF_3C_6H_4$

**12**

Figure 1. ORTEP drawing of **11**.

Thermolysis of **10a,b** at 180 °C in a toluene-$d_8$ solution in the presence of $Ph_3P{=}O$ and $EtO_2CNHNHCO_2Et$ as products gave a trace of styrene. When **11** ($\delta(^{31}P)$ -29.9) was dissolved in toluene-$d_8$, another signal appeared at $\delta(^{31}P)$ -50.9, probably due to pseudorotamer **13** with the nitrogen being equatorial.[9] Heating of the solution at 200 °C for 5 d in a sealed tube gave quantitatively 1,1-diphenylethylene and the corresponding iminophosphorane **14**, which was hydrolyzed to the corresponding cyclic phosphinate **15** along with aniline.






REFERENCES


1 a) T. Kawashima, K. Kato, and R. Okazaki, J. Am. Chem. Soc., 114, 4008 (1992); b) T. Kawashima, K. Kato, and R. Okazaki, Angew Chem., Int. Ed. Engl., 32, 869 (1993);
2. T. Kawashima, N. Iwama, and R. Okazaki, J. Am. Chem. Soc., 114, 7598 (1992).
3. T. Kawashima, Y. Nishiwaki, and R. Okazaki, J. Organomet. Chem., in press.
4. T. Kawashima, N. Iwama, and R. Okazaki, J. Am. Chem. Soc., 115, 2507 (1993).
5. H. J. Bestmann and F. Seng, Angew. Chem., 75, 475 (1965).
6. The Martin ligand was introduced by using the dithio derivative of hexafluorocumyl alcohol: E. F. Perozzi, R. S. Michalak, G. D. Finguly, W. H. Stevenson, III, D. B. Dess, M. R. Ross, and J. C. Martin, J. Org. Chem., 46, 1049 (1981).
7. For a review, see: O. Mitsunobu, Synthesis, 1981, 1.,
8. H. W. Roesky, K. Ambrosius, M. Banek, and W. S. Sheldrick, Chem. Ber., 113, 1847 (1980).
9. NOE observed between the *ortho*-proton of the Martin ligand and one of 3-methylene protons indicates that two protons are close to each other, which is possible only in the case of the methylene-apical pseudorotamer.