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Accounts

Syntheses, Structures, and Thermolyses of Three- and Four-Membered Heterocyclic Compounds Containing Highly Coordinate Main Group Elements

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Most titled compounds were synthesized by taking advantage of the Martin ligand. Their structures were determined by X-ray crystallography. Thermolyses of most of the four-membered ring compounds gave the corresponding Wittig-type products, while those of 1,2-oxasiletanides in the presence of proton source afforded the homo-Brook rearrangement products depending on bulkiness of the substituent at the 3-position. Pentacoordinate thiasiliranides were hydrolyzed to give the corresponding thiol, which seems to be formed via the initial cleavage of the Si–C bond followed by further hydrolysis of the corresponding thia-Brook rearrangement product. On the other hand, the most polarized bond of a pentacoordinate selenaphosphirane was found to be the P–Se bond, which was confirmed by its reaction with CF_3SO_3Me to give the corresponding 1-(methylseleno)alkylphosphonium triflate and by the solvent-dependent NMR study.

Four- and three-membered heterocyclic compounds containing highly coordinate main group elements at the position adjacent to the heteroatom have received much attention, because of their unique structures and reactivity. Particularly, four-membered heterocycles containing an oxygen and a pentacoordinate phosphorus atom and three-membered ones with an oxygen and a pentacoordinate silicon atom have been considered as intermediates of the Wittig reaction and the Brook rearrangement, respectively; these are a very useful synthetic organic reaction and a typical reaction of organosilicon chemistry, respectively.[1,2]

In the course of our study on such heterocyclic compounds, we have succeeded in the syntheses of intermediates of the Wittig reaction,[3] the Peterson reaction,[4] and the boron-Wittig reaction,[5] most of which were obtained as stable compounds by taking advantage of stabilization effects of the Martin ligand.[6] We have also reported that some of the group 16 element analogues, which have the structures similar to those of group 14 and 15 element analogues, afforded the corresponding oxiranes with retention of configuration.[7] Furthermore, we have also synthesized spiro compounds bearing two 1,2-oxaheteretane rings and demonstrated that these compounds, namely, 2,2′-spirobi[1,2-oxaphosphetane],[8] 2,2′-spirobi[1,2-oxasiletanide],[9] and 2,2′-spirobi[1,2-oxaselenetane],[10] undergo double alkene, oxirane, and alcohol formation reactions, respectively. These results were described in previous accounts and reviews.[11] In the present account, we wish to summarize our recent results concerning four- and three-membered heterocycles containing highly coordinate main group elements, together with some of our previous results.[12]

1. Four-Membered Heterocyclic Compounds Containing Two Heteroatoms

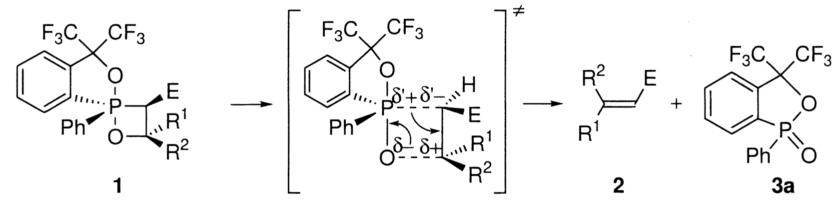
1.1 Pentacoordinate 1,2-Oxaphosphetanes, Intermediates of the Wittig Reaction. Thanks to large contributions of Wittig and many other synthetic chemists, the Wittig reaction has been widely utilized as one of the excellent methods for the synthesis of alkenes and as a key-step of the synthesis of natural products.[1]

Since Wittig reported that the corresponding (2-hydroxyalkyl)phosphonium salt was obtained by quenching the Wittig reaction with an acid at low temperature, the mechanism including a betaine and an oxaphosphetane as an intermediate and a transition state, respectively, has been generally accepted. Although several isolable pentacoordinate $1,2\lambda^5$-oxaphosphetanes have been reported,[13] Vedejs and Maryanoff and their co-workers observed directly pentacoordinate 1,2-oxaphosphetane by low temperature ^{31}P NMR spectroscopy in the Wittig reaction of salt-free non-stabilized ylides with aldehydes. It was found that these intermediates are the only detectable products of the reaction and that (*Z*)- and (*E*)-alkenes were formed stereospecifically from intermediary *cis*- and *trans*-oxaphosphetanes, respectively, but in some cases the ratio of geometric isomers of the alkene did not agree with that of *cis*-

and *trans*-oxaphosphetanes (stereochemical drift).[1d,e] These compounds could not be isolated, even if they are thermally stable, probably because of their high moisture-sensitivity. Very recently, the first stable *cis*-oxaphosphetane was synthesized by introduction of heteroaromatic substituents such as a 2-furyl group on the phosphorus and its structure was determined by X-ray crystallographic analysis.[14]

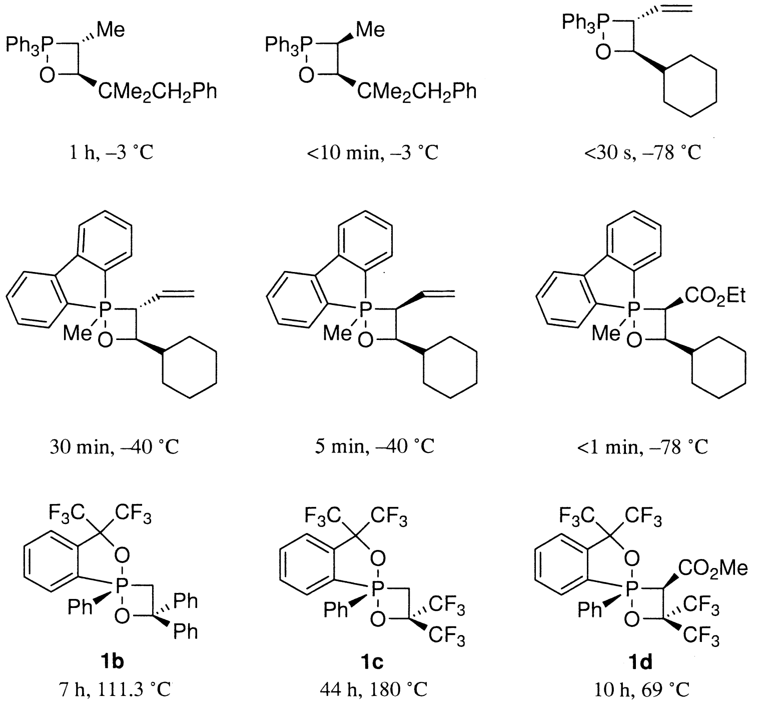
We synthesized pentacoordinate 1,2-oxaphosphetanes **1a-d** bearing the Martin ligand (Scheme 1).[3] 3-Methoxycarbonyl-1,2-oxaphosphetane **1d** is considered as a formal [2 + 2]-cycloadduct of a stabilized phosphorus ylide with a carbonyl compound, which has never been observed even spectroscopically in spite of many efforts.[1c,d] X-ray crystallographic analyses of **1a** and **1d** revealed that they have slightly distorted trigonal bipyramidal (TBP) structures, with two oxygen atoms at the apical positions and three carbon atoms at the equatorial positions.[3a,c] Their thermolyses quantitatively gave the corresponding alkenes **2** and cyclic phosphinate **3a**. Our kinetic studies of the thermolysis of **1** found that the alkene formation from these 1,2-oxaphosphetanes, the second step of the Wittig reaction, proceeds via a slightly polar transition state (Scheme 1). The relative rates at 111.3 °C were calculated to be 1 : 11,400 : 478,000 (**1c** : **1b** : **1d**), indicating that the alkene formation was largely accelerated by the introduction of a methoxycarbonyl group at the 3-position. Comparing half lives (Scheme 2) of **1c**, **1b**, and **1d** calculated from the kinetic data with those of other compounds,[1e,11d] one may reasonably conclude that the Martin ligand can stabilize this type of compounds very well. Recently, we have found that the reaction of the in-situ generated phosphorus ylide **4a** bearing the Martin ligand with benzophenone gives **1b** in a 72% yield (Scheme 3) and hence we have succeeded in realizing each step of the Wittig reaction in this system.[15]

Most pentacoordinate 1,2-oxaphosphetanes have the four membered rings with the oxygen at the apical position and the carbon at the equatorial position, except for a ring-fused spirophosphorane **5**.[16] Recently, C-apical oxaphosphetane **6a** was isolated as a kinetic-controlled product of oxidative cyclization

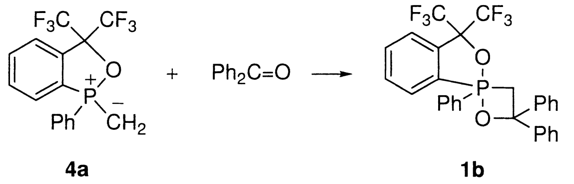


a: E = H, $R^1 = R^2 = p\text{-}FC_6H_4$
b: E = H, $R^1 = R^2 = Ph$
c: E = H, $R^1 = R^2 = CF_3$
d: $E = CO_2Me$, $R^1 = R^2 = CF_3$

Scheme 1.

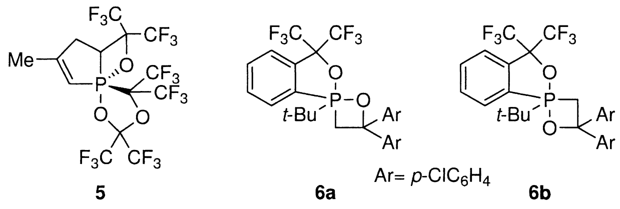


Scheme 2. Qualitative half lives for Oxaphosphetane Decomposition.



Scheme 3.

of the corresponding hydro(2-hydroxyalkyl)phosphorane and its structure was determined to be essentially of TBP nature by X-ray analysis.[17] It was found that heating **6a**, which has been considered as a reactive intermediate of the Wittig reaction, gave only O-apical **6b** as a consequence of pseudorotation and that only after prolonged heating of **6b** could alkene formation be observed, indicating that the transition state of the direct alkene formation from **6a** is much higher in energy than that of stereomutation (Scheme 4).



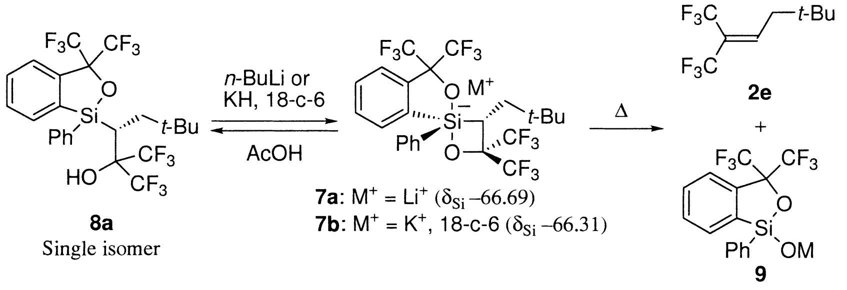
Scheme 4.

1.2 Pentacoordinate 1,2-Oxasiletanides, Intermediates of the Peterson Reaction and the Homo-Brook Rearrangement. The Peterson reaction using silyl stabilized carbanions and carbonyl compounds is well-known as a silicon analogue of the Wittig reaction.[18] It provides an important methodology for the stereospecific formation of (*E*)- and (*Z*)-alkenes from a single diastereomer of (2-hydroxyalkyl)silanes by changing reaction conditions (acidic vs basic).[19] Peterson-type reactions using carbanions adjacent to other group 14 elements such as Ge, Sn, and Pb have been also reported.[20] On the other hand, protiodesilylation-type alcohol formation from a (2-hydroxyalkyl)silane under basic conditions in the presence of a proton source is known as the homo-Brook rearrangement.[21] Hudrlik and co-workers proposed a plausible mechanism of this reaction, which involves a pentacoordinate 1,2-oxasiletanide.[22] The above-mentioned successful syntheses of pentacoordinate 1,2-oxaphosphetanes as stable compounds prompted us to synthesize a pentacoordinate 1,2-oxasiletanide as an isolable compound by the introduction of the Martin ligand. We succeeded in the synthesis of an intermediate of the Peterson reaction.[4] In connection with this study, a pentacoordinate 1,2-oxasiletanide was found to have some reactivity as an intermediate of homo-Brook rearrangement as, described below.[11e,23]

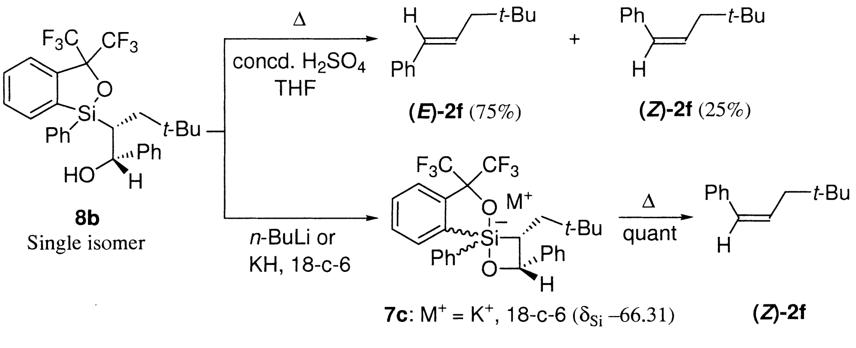
Deprotonation of (2-hydroxyalkyl)silane **8a** gave the first pentacoordinate 1,2-oxasiletanides **7a** and **7b**, which gave quantitatively the corresponding alkene **2e** and **9** upon heating (Scheme 5).[4] The structure of **7b** was determined by X-ray crystallographic analysis.

Treatment of a single diastereomer **8b** with KH in the presence of 18-crown-6 gave **7c** as a 2:1 mixture of two diastereomers based on the stereochemistry of central silicon atom. Upon heating at 50 °C, **7c** afforded (*Z*)-**2f** exclusively and quantitatively, whereas treatment of **8b** with a few drops of concd. H_2SO_4 in THF gave mainly (*E*)-**2f**, indicating that this system also has a typical feature of the Peterson reaction (Scheme 6). The significant stereochemical drift is probably due to syn-elimination of the alkene from the corresponding tetracoordinate 1,2-oxasiletane formed by O-protonation of the Martin ligand followed by the Si–O bond cleavage.[24]

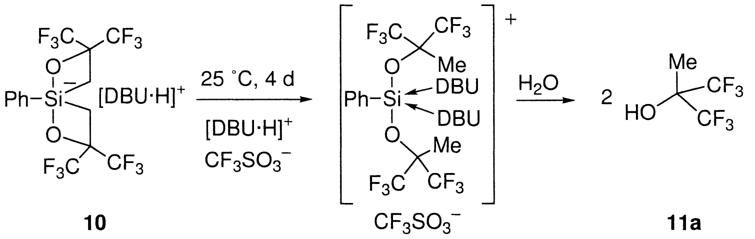
On the other hand, 2,2′-spirobi[1,2-oxasiletanide] **10** gradually decomposed at 25 °C to give almost quantitatively alcohol **11a** after treatment with water (Scheme 7).[9] In this sense, pen-



Scheme 5.



Scheme 6.



Scheme 7.

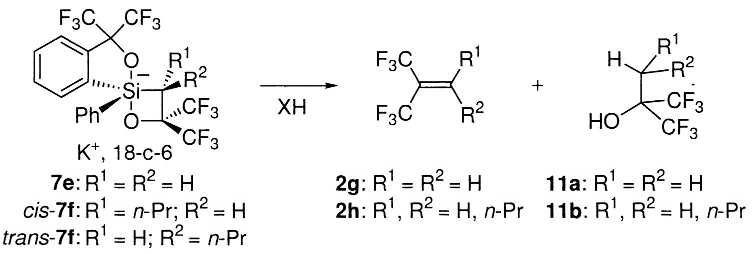
tacoordinate silicate **10** can be regarded as the first example of a detectable intermediate of homo-Brook rearrangement. It is very interesting that the pentacoordinate 1,2-oxasiletanides bearing the Martin ligand and 2,2′-spirobi[1,2-oxasiletanide] indicated different reactivity valves, whereas they have the same partial structure. There are differences between them both in the substituent at the 3-position of the 1,2-oxasiletanide ring and in the ring system. Therefore, it is necessary to compare the reactivities between the compounds that have different substituents only at the 3-position of the 1,2-oxasiletane ring. We decided to use the ring system with the Martin ligand for the purpose of elucidating factors controlling two reaction modes: the Peterson reaction and the homo-Brook rearrangement.[11e,23]

3-Unsubstituted derivative **7e** and 3-propyl derivatives **7f** were similarly obtained as a single isomer and an inseparable mixture of two diastereomers *cis*-**7f** and *trans*-**7f**, in which the phenyl group on Si and the propyl group are *cis* and *trans*, respectively.

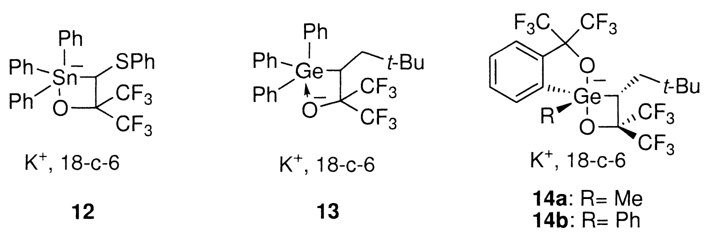
Thermolyses of **7b**, **7e**, and **7f** were carried out in the presence of proton sources such as methanol, 2,2,2-trifluoroethanol, and acetic acid (Scheme 8). The corresponding alkene **2e** was formed in thermolysis of **7b** and the alcohol was not obtained at all. In the cases of thermolyses of **7e** and **7f**, the ratio of alkene **2** to alcohol **11** significantly decreased with an increase of the acidity of the proton source. In the presence of acetic acid, thermolysis of **7f** gave a small amount of alcohol **11b**, while that of **7e** predominantly afforded alcohol **11a** even in the presence of 2,2,2-trifluoroethanol.

Considering these results, one can determine the selectivity of two reaction modes (alkene formation vs. alcohol formation) as follows. Alcohol **11** is formed only in the reaction of pentacoordinate 1,2-oxasiletanides that have small substituents at the 3-position in the four-membered ring in the presence of a proton source that has relatively high acidity. If a bulky group exists at this position, alkene **2** is formed because the protonation of the negatively charged carbon, which would be generated by elongation of the Si–C bond in the oxasiletanide ring, is encumbered by the bulky group. Propyl and neopentyl groups are considered to have a similar electronic character. But the reaction of pentacoordinate 1,2-oxasiletanide **7f** affords the alcohol in the presence of acetic acid, while thermolysis of **7b** gives only the alkene under the same conditions. Therefore, the steric factor is important for the determination of the reaction modes. Thus, it was demonstrated that pentacoordinate 1,2-oxasiletanides undergo two reactions: the Peterson reaction and the homo-Brook rearrangement.

1.3 Pentacoordinate 1,2-Oxagermetanides and 1,2-Oxastannetanides. We have also synthesized intermediates of the germanium-Peterson and the tin-Peterson reactions (Scheme 9).[25] Without resort to the Martin ligand, pentacoordinate 1,2-oxastannetanide **12** could be synthesized as a stable com-



Scheme 8.



Scheme 9.

pound, which has a distorted structure close to square pyramidal (SP).[25a] The crystal structure of germanium compound **13** was interpreted as a germyl alkoxide with strong interaction between oxygen and germanium atoms.[25b] Oxagermetanides **14a** and **14b** with a distorted TBP structure could be synthesized by the introduction of the Martin ligand into the system.[25c] Interestingly, thermolyses of **12**, **13**, **14a**, and **14b** gave the corresponding alkenes finally in quantitative yields regardless of the difference in their structures. It must be pointed out that 1,2-oxagermetanide **14b** with the Martin ligand undergoes isomerization by pseudorotation before the Wittig-type cleavage, in sharp contrast to its silicon analogue **7b**, probably because of its lower barrier of pseudorotation compared with **7b**.[25c]

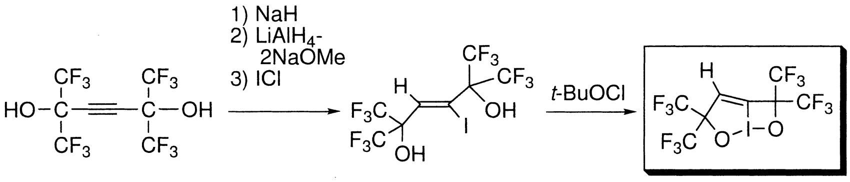
1.4 A Tricoordinate 1λ^3,2-Iodoxetane. Ochiai and coworkers reported that the reactions of an iodonium ylide with aldehydes afford the corresponding oxiranes.[26] These results prompted us to investigate an oxetane having a tricoordinate iodine, i.e., a group 17 element analogue, which remains still unknown even though several hypervalent iodine compounds are utilized as reagents for organic synthesis.[27,28] We reported the synthesis, structure, and reactions of tricoordinate 1λ^3,2-iodoxetane **15**,[29] formal [2 + 2]-cycloadduct of an iodonium ylide with a carbonyl compound, using a novel ligand which was designed for that compound.[30]

Tricoordinate 1λ^3,2-iodoxetane **15** was synthesized from **16** via **17** as pale yellow crystals (Scheme 10) and its structure was determined by X-ray crystallographic analysis. This is the first example of a tricoordinate 1λ^3,2-iodoxetane.[29]

X-ray analysis showed that it has a distorted T-shape structure with two oxygen atoms at the apical positions. The intermolecular distance between the iodine and the oxygen of the four-membered ring is 2.821(3) Å, which is much shorter than the sum of van der Waals radii (3.55 Å), indicating a dimeric structure of **15** similarly to **18** (Scheme 11).[31] The four-membered ring is almost planar, judging from the torsion angle I–C–C–O 0.0(3)° and the sum of the bond angles of the four-membered ring (359.9°), which is a typical feature of most of oxetanes bearing highly coordinate main group elements.[11]

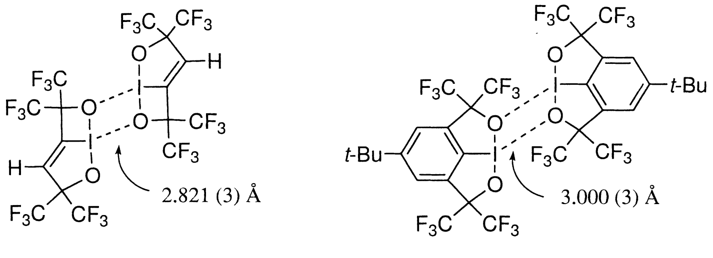
Thermolysis of **15** (CD_3CN) gave almost quantitatively **16** together with a trace of **17** (Scheme 12). A plausible formation mechanism of **16** and **17** is as follows: heterolysis of the I–O bond takes place to give iodonium oxide **19**, which undergoes intramolecular or intermolecular deprotonation with elimination of I–O group to give hypoiodite **20** because of high leaving ability of iodonio groups, as demonstrated by Stang and Ochiai.[27,32] Homolytic cleavage of I–O bond of **20** gives the alkoxyl radical **21** and I$^\bullet$, which abstracts deuterium from CD_3CN to give **16-*d*** and DI, respectively. **15** was reduced with 2DI to give **17-*d*$_2$** and I_2 (Scheme 13). The oxidizing ability of **15** was also demonstrated by the reaction with benzyl alcohol, giving benzaldehyde together with (*E*)- and (*Z*)-**17**.

Unfortunately, the above-mentioned competitive reaction took place and hence no information on the expected thermal



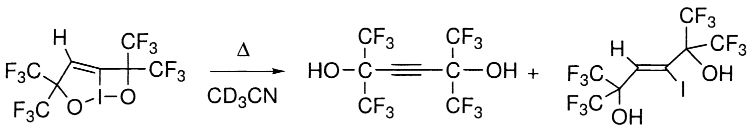
16 **17** **15**

Scheme 10.



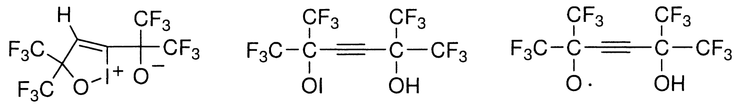
15 **18**

Scheme 11. Dimeric structures of **15** and **18**.



15 **16** **17**

Scheme 12.



19 **20** **21**

Scheme 13.

reactivity, i.e., alkene or oxirane formation, was obtained.

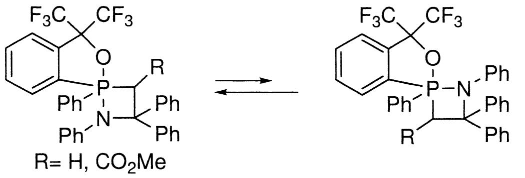
2. Four-Membered Heterocyclic Compounds Containing Three Heteroatoms

2.1 Pentacoordinate 1,3,2λ^5-Oxazaphosphetidines, Intermediates of Aza-Wittig Reaction. Iminophosphoranes have been explored in connection with phosphonium ylides, providing aza-Wittig reactions, which have been utilized as effective methods for the synthesis of nitrogen-containing heterocycles.[33] For the elucidation of the mechanism of aza-Wittig reactions, it is valuable to isolate their intermediates, i.e., 1,3,2λ^5-oxazaphosphetidines, because such isolation can provide direct evidence about its mechanism. Furthermore, taking into consideration the polarized electronic structure of an iminophosphorane, we expect it to be an useful building block of small-membered ring compounds. In the course of our study on the reactivities of an iminophosphorane bearing the Martin ligand, we reported the formation of 1,3,2λ^5-oxazaphosphetidine **22**, which is the first example of dioxyaminophosphorane [10-P-5(C_2O_2N)] with a 1,3,2-oxazaphosphetidine ring, by the reaction of iminophosphorane **23** with carbonyl compounds.[34,35] The thermolysis of the four-membered ring compound **22a** revealed the formation of the Wittig-type products and the existence of equilibrium with the starting materials. We used the Martin ligand and a bulky 2,4,6-triisopropylphenyl (denoted as Tip hereafter) group for the stabilization of the cycloadducts.

Moisture-sensitive iminophosphorane **23** was allowed to react with hexafluoroacetone (HFA) at room temperature to give the corresponding 1,3,2λ^5-oxazaphosphetidine **22a** as a colorless crystal after chromatographic separation (Scheme 14).[34] X-ray crystallographic analysis revealed that **22a** has a distorted TBP structure with two oxygen atoms at the apical positions and two carbon and one nitrogen atoms at the equatorial positions. It is noteworthy that **22a** was obtained from the iminophosphorane, which was generated from the corresponding phosphine and azide as reported for the general aza-Wittig reactions, in marked contrast to the previously reported 1,3,2λ^5-oxazaphosphetidines,[36] which required indirect methods of preparation. The reactions of iminophosphorane **23** with benzaldehyde and trifluoroacetophenone at 60 and 70 °C also afforded 1,3,2λ^5-oxazaphosphetidines **22b** and **22c**, respectively, as the diastereomeric mixtures. Unfortunately, 1,3,2λ^5-oxazaphosphetidines **22b** and **22c** could not be isolated, because they were easily hydrolyzed on silica gel (Scheme 14).

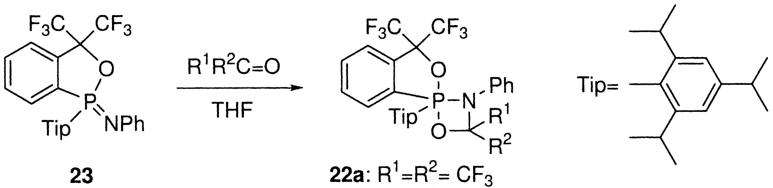
An N-apical pseudorotamer of **22a** was not detected by variable temperature NMR spectra between 27 °C and 107 °C, although N-equatorial pseudorotamers that violate the apicophilicity rule were observed at room temperature for 1,2-azaphosphetidines **24** (Scheme 15).[37] This is interesting because the difference in electronegativity between oxygen and nitrogen atoms for **22a** is almost the same as that between carbon and nitrogen atoms for **24**. Thus, the reason why an N-apical pseudorotamer was not observed is because of the steric bulkiness of one of equatorial substituents of **22a**.

Thermolysis of **22a** afforded imine **25** (90%) and cyclic phosphinate **3b** (100%) (Scheme 16). Furthermore, the 1,3,2λ^5-oxazaphosphetidine is expected to exhibit another reaction mode on the thermolysis, i.e., the formation of the iminophosphorane as in the cases of the 1,2-azaphosphetidines.[37] Since this process must be reversible, it must be made irreversible by some method in order to confirm the existence of this process. We know iminophosphorane **23** is very sensitive to moisture, so that thermolysis in the presence of water was carried out. In fact, thermolysis of **22a** with an excess amount of water gave almost quantitatively HFA, **3b**, and aniline. Since imine **25** was stable under the reaction conditions, the thermolysis process of **22a** giving HFA and **23** was evidenced by formation of HFA, **3b**, and aniline. The formation of **23** was also confirmed by trapping with methanol to give methanol adduct **26**. These results indicate two reaction pathways for the thermolysis of **22a**: one is formation of the aza-Wittig reaction



N-apical pseudorotamer N-equatorial pseudorotamer

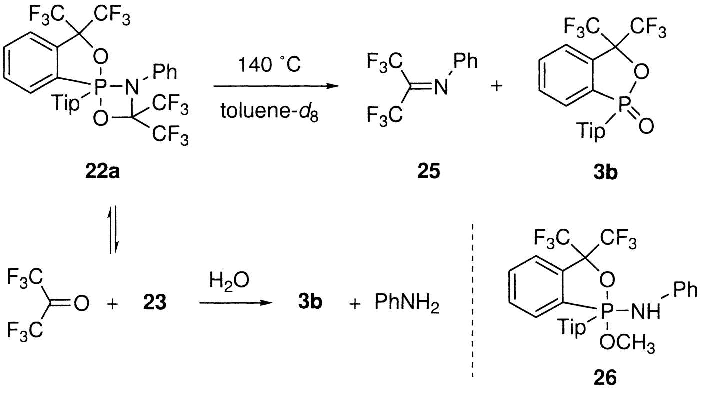
Scheme 15. Pseudorotamers of 1,2λ^5-azaphosphetidines **24**.



23

22a: $R^1=R^2=CF_3$
22b: R^1, R^2= Ph, H
22c: R^1, R^2= Ph, CF_3

Scheme 14.



Scheme 16.

products, imine **25** and cyclic phosphinate **3b**, and the other is regeneration of iminophosphorane **23** and HFA. Since the former path is the second step of the aza-Wittig reaction, 1,3,2λ^5-oxazaphosphetidines **22** can be regarded as intermediates of the aza-Wittig reaction.

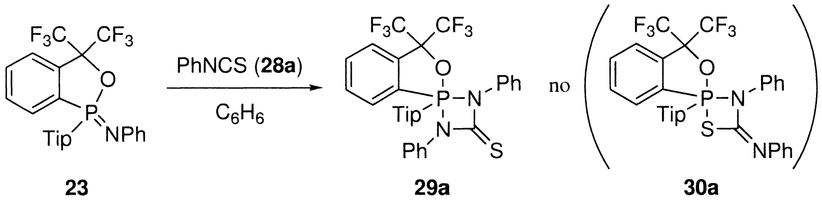
2.2 Pentacoordinate 1,3,2λ^5-Diazaphosphetidine-4-thione. There has been only one report on the X-ray crystallographic analysis of a 1,3,2λ^5-thiazaphosphetidine ring to date.[38] The formation and isolation of 1,3,2λ^5-oxazaphosphetidine **22a** bearing the Martin ligand as an isolable solid encouraged us to study the cycloaddition reactions with carbon–sulfur double-bond compounds in anticipation of the formation of the 1,3,2λ^5-thiazaphosphetidines. An attempted reaction of iminophosphorane **23** with thiobenzophenone resulted in no reaction, while monitoring the reaction of **23** with carbon disulfide in C_6D_6 at 60 °C afforded the cyclic thiophosphinate **27** without an observable intermediate. On the other hand, the reaction of **23** with phenyl isothiocyanate (**28a**) in benzene at 50 °C gave the corresponding 1,3,2λ^5-diazaphosphetidine-4-thione **29a** instead of 1,3,2λ^5-thiazaphosphetidine **30a** (Scheme 17).

X-ray crystallographic study revealed that **29a** has a distorted TBP structure with an oxygen and a nitrogen atom at the apical positions. It makes a contrast to the nearly SP structure of the previously reported pentacoordinate 1,2-diazaphosphetidine-4-thione.[39]

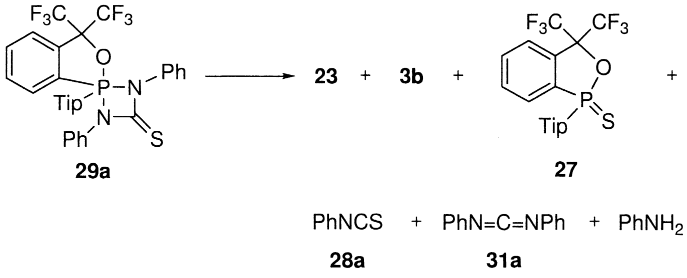
Thermolysis of 1,3,2λ^5-diazaphosphetidine-4-thione **29a** afforded iminophosphorane **23**, cyclic phosphinate **3b**, and cyclic thiophosphinate **27** (Scheme 18). Formation of **28a**, carbodiimide **31a**, and aniline was also confirmed by GC-MS spectra.

From the results of the reaction of **23** with excess *p*-tolyl isothiocyanate, the formation of carbodiimide **31a** can most likely be explained as shown in Scheme 19.

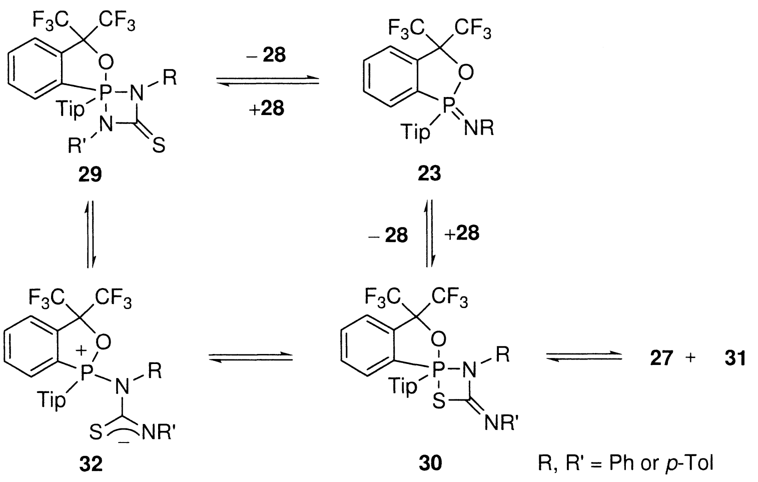
Upon heating, **29** is firstly expected to undergo the cycloreversion giving **23** and isothiocyanate **28**. The sequential [2+2]-cycloaddition of the P=N unit of **23** with C=S unit of the isothiocyanate gives the intermediary **30**, which affords cyclic thiophosphinate **27** and carbodiimide **31**. For the formation of **30**, the P–N bond dissociation of **29** followed by intramolecular P–S bond formation of the thus obtained zwitterion **32** is also considered as another mechanism. The present formation of cyclic thiophosphinate **27** and carbodiimide **31** from 1,3,2λ^5-thiazaphosphetidine **30** is considered to proceed via P–N bond dissociation, in marked contrast to the reactivity of Schmidpeter's 1,3,2λ^5-diazaphosphetidine-4-thiones, which rearrange intramolecularly but do not give the corresponding P=S and carbodiimide units.[40]



Scheme 17.



Scheme 18.



Scheme 19.

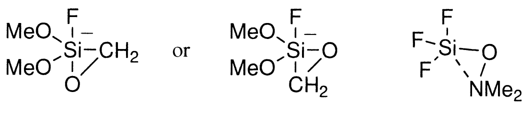
3. Three-Membered Heterocyclic Compounds Containing Two Heteroatoms

3.1 Pentacoordinate $1,2\lambda^5$-Thiasiliranides. The Brook rearrangement is an intramolecular 1,2-migration of silicon from carbon to oxygen (forward Brook rearrangement) or from oxygen to carbon (reverse Brook rearrangement). Such a migration has been considered to proceed through a three-membered ring compound bearing a pentacoordinate silicon at the position adjacent to an oxygen atom, i.e., a pentacoordinate oxasiliranide (Scheme 20 (X=O)).[2] For the thia-Brook rearrangement (Scheme 20 (X=S)), the forward one has rarely been reported, in contrast to the reverse one that easily proceeds.[41] But the first example for the forward thia-Brook rearrangement was reported in the reaction using methyllithium as base.[42]

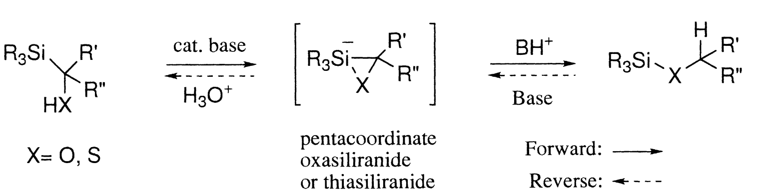
The $FSi(OCH_3)_2(OCH_2)^-$ ion was observed as a minor product in the gas-phase ion/molecule reaction of $Si(OMe)_4$ with F^- and this molecule was suggested to be pentacoordinate oxasilirane species **33a** or **33b** by its reactivity and theoretical calculation (Scheme 21).[43] To the best of our knowledge, three-membered ring compounds containing a pentacoordinate silicon whose structures were definitively determined are only **34** and its related compounds (Scheme 21).[44] Neither isolation nor spectroscopic observation of oxa- or thia-siliranides in solution has been reported.[41] These compounds are also interesting compounds from viewpoints of their unique structures as pentacoordinate organosilicon species containing a small membered ring. As mentioned above, we succeeded in the synthesis of pentacoordinate 1,2-oxasiletanides, which are stabilized by the Martin ligand. These results prompted us to investigate three-membered ring compounds with the Martin ligand.[45]

An inseparable mixture of two diastereomers **35a** and **35b**, whose stereochemistry could not be determined, was treated with potassium hydride in the presence of 18-crown-6 to give the corresponding pentacoordinate thiasiliranides **36** (Scheme 22), while that of 1-silyl-1-alkanethiol **37** without the Martin ligand afforded thiolate anion **38**, judging from degree of upfield shifts in ^{29}Si NMR.

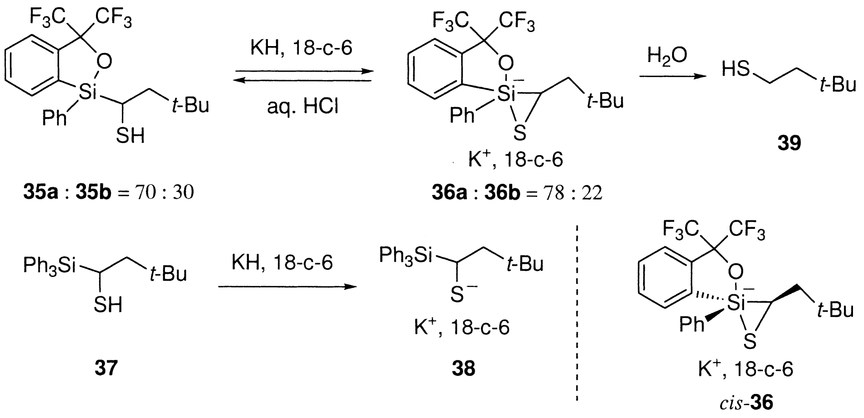
X-ray crystallographic analysis of one isomer of pentacoordinate thiasiliranides **36a** and **36b** indicated that the phenyl group on the silicon is *cis* to the neopentyl group and that it has a very distorted TBP structure, with oxygen and sulfur atoms at apical positions and three carbon atoms at equatorial positions (Scheme 22). This is the first example of X-ray crystallographic analysis of a pentacoordinate thiasiliranide, and moreover, the first example of a pentacoordinate silicate containing a three-membered ring. The bond length of Si–S (2.569(9) Å) is substantially longer than those observed in bis(triphenylsilyl) sulfide (2.152(2) Å),[46] tetracoordinate thiasilirane [$–CMe_2$-$C_6H_4CMe_2–$]Si[$–SSiMes_2–$] (2.093 Å)[47] and the sum of the covalent bond radii (2.20 Å). But, taking into consideration that the Si–S bond is apical bond and that the apical bond in pentacoordinate silicate is generally ca. 10% longer than the same bond in tetracoordinate silicon compound, we consider the Si–



Scheme 21.



Scheme 20. Brook-type rearrangement.



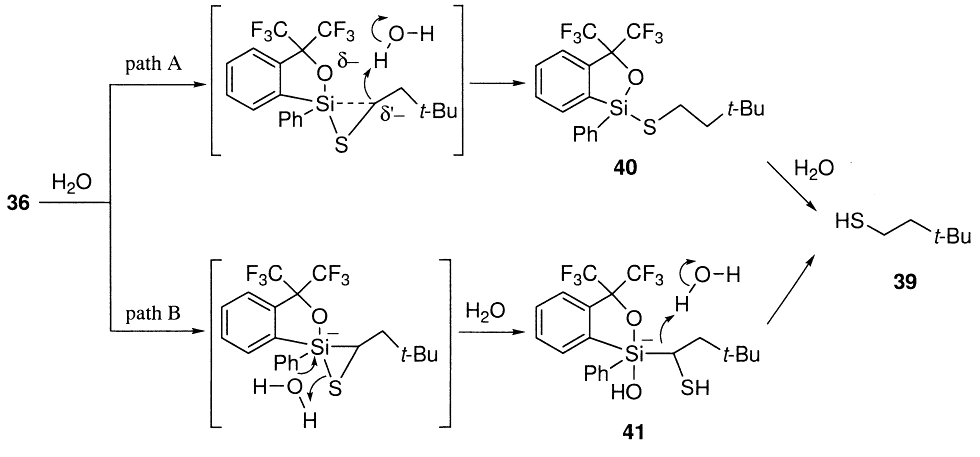
Scheme 22.

S bond length of *cis*-**36** (2.57 Å) to be a reasonable value. The Si–C–S bond angle is 87.4(10)°, which is significantly smaller than the tetrahedral angle (109.5°), supporting the existence of Si–S interaction. This striking feature was also observed in (*N*,*N*-dimethylaminoxy)trifluorosilane **34** having β-donor interaction.[44e] Moreover, the sum of three equatorial angles is 350°, which is closer to that of ideal TBP structure (360°) than that of ideal tetrahedral structure (328°). The distance (3.12 Å) between K and S is shorter than the sum (4.55 Å) of the van der Waals radii of K and S, indicating the significant interaction between K and S in the solid state, but *cis*-**36** is thought to retain a pentacoordinate structure, judging from the above discussion on the bond angles.

Pentacoordinate thiasiliranides **36a** and **36b** are unstable against moisture. They were hydrolyzed immediately to give 3,3-dimethylbutanethiol (**39**). On the other hand, treatment of a mixture (78:22) of **36a** and **36b** with an excess amount of hydrochloric acid gave a mixture (70:30) of two diastereomers of 1-silyl-1-alkanethiols **35a** and **35b** (Scheme 22).

Two reaction mechanisms can be proposed for the formation of thiol **39**, that is, C-protonation mechanism (path A) and S-protonation mechanism (path B) (Scheme 23). In path A, at first the protonation takes place on negatively charged carbon, which would be generated by elongation of the Si–C bond in the thiasilirane ring. Hydrolysis of alkylthiosilane **40** thus obtained gave thiol **39** (reactivity as intermediates of the Brook rearrangement). On the other hand, the protonation to sulfur atom is assumed to occur at first in path B. Simultaneously, nucleophilic attack of HO^- to silicon center occurs to give a pentacoordinate silicate **41**. Further hydrolysis of **41** is considered to give thiol **39**. However, protonation on the sulfur with water must be reversible, because thus-formed hydoxide is a base strong enough to deprotonate from the SH group. The fact that **35** were obtained by the reaction of **36** with hydrochloric acid strongly suggests that first protonation occurs on the sulfur atom of pentacoordinate thiasiliranides. Further investigation would be necessary for determining the reaction pathway.

3.2 1,2σ^5-Selenaphosphirane. Three-membered ring compounds containing phosphorus have been studied for four decades both experimentally and theoretically, in view of their interesting structural features and high strain energies.[48] Although many examples bearing a tri- and tetra-coordinate phosphorus atom, such as phosphiranes, as well as those containing another heteroatom in the ring were synthesized and their structures and properties were established,[49] there are only limited reports on three-membered ring compounds bearing a phosphorus atom with a coordination number higher than four.[50,51] Some σ^5(P)-phosphirenes bearing a C–C double bond in the ring were synthesized and some of them were crys-



Scheme 23.

tallographically characterized,[50c] but only a few compounds bearing a pentacoordinate phosphorus atom located in the saturated three-membered ring have been reported to date.

On the other hand, reactions of phosphorus ylides with elemental sulfur are known to give the corresponding phosphine sulfides and thioketones (the Staudinger reaction) and those with elemental selenium have been considered to afford the corresponding selenoketone as intermediates via cyclic polychalcogenides containing a pentacoordinate phosphorus.[52,53] Such species can be stabilized by introduction of the Martin ligand. We tried the reaction of a phosphorus ylide bearing the Martin ligand with elemental selenium.[54]

Treatment of **4b** bearing the Martin ligand, which was prepared from the corresponding fluorophosphorane **42** via phosphonium triflate **43**,[55] with elemental selenium in THF at room temperature successfully afforded selenaphosphirane **44** as a colorless and moisture-sensitive solid (Scheme 24).[52e–h]

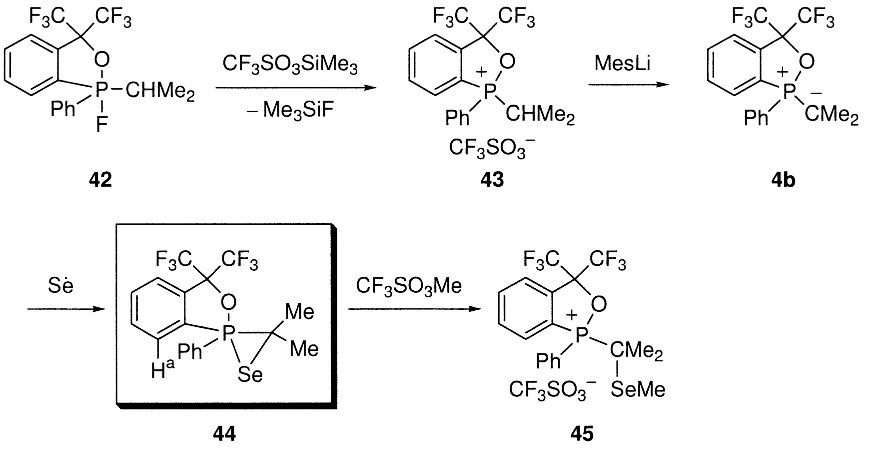
The molecular structure of **44** was established by X-ray crystallographic analysis. The apical bond angle O–P–Se (155.82(6)°) and the apical-equatrorial angle O–P–C (102.61(10)°) are far from those of a TBP structure (%TBP→SP: 56).[56] If one judges from the value of %TBP character, **44** exhibits an intermediate structure between TBP and square pyramidal. The P–Se bond length (2.4540(10) Å) is much shorter than the sum of van der Waals radii of phosphorus and selenium (3.9 Å), which indicates the interaction between the phosphorus and selenium atoms of **44** in the crystalline state. The P–C–Se angle (81.13(10)°) is significantly reduced from the bond angle of a tetrahedral structure (109.5°) and the C–P–Se angle (53.53(8)°) deviates from a TBP structure (90°), respectively. These structural features clearly suggest the formation of the P–C–Se three-membered ring structure of **44**. This is the first example of an X-ray structural analysis of not only a selenaphosphirane, but also a saturated three-membered ring compound involving a pentacoordinate phosphorus atom.

In the solid-state $^{31}P\{^1H\}$ NMR spectrum, **44** showed a singlet at δ_P −26.1, whereas in the C_6D_6 solution, the signal of **44** in the $^{31}P\{^1H\}$ NMR spectrum was observed at δ_P −26.6 as a singlet, suggesting the pentacoordinate state of the phosphorus atom of **44** to persist also in C_6D_6. Although the spin-spin coupling between the phosphorus and the selenium nuclei was observed in the cases of 1,2σ^3-selenaphosphiranes,[49d,f,l] **44** showed no spin-spin coupling between these two nuclei. The reason for the absence of the spin-spin coupling in **44** is unclear at present.

In the solution state, **44** showed an interesting behavior depending on acceptor numbers of the solvents. Since the ^{31}P resonances of **44** in these solvents still appeared at high field, the phosphorus atom of **44** should retain the pentacoordinate state in these solvents.[57] A rough correlation was found between the acceptor numbers of the solvents and the ^{31}P and ^{77}Se NMR shifts of **44**.[58] The larger the acceptor number becomes, the lower the field at which the signal of **44** appeared in the ^{31}P NMR spectrum and the higher the field in the ^{77}Se NMR spectrum, respectively. Moreover, the signal of Ha as shown in Scheme 24 is shifted to lower field in ^1H NMR with increasing the acceptor number. These results show that the negative charge on the selenium atom and the positive charge on the phosphorus atom increase with increasing acceptor number of the solvent, that is, the polarization of the P–Se bond depends on the acceptor number of the solvent. Treatment of **44** with 2 molar amounts of methyl triflate in $CDCl_3$ gave the highly air-sensitive (1-methylselenoalkyl)phosphonium triflate **45**. The formation of **45** was reasonably explained by the electrophilic attack of methyl triflate on the negatively charged selenium atom of **44** and the subsequent dissociation of the P–Se bond, reflecting the polarized character of the P–Se bond. The reason why three-membered ring compound **44** was obtained in the present reaction is the steric congestion around the central phosphorus, which may allow only three-membered rings to form.

4. Conclusion

We have described our recent results concerning isolable four-membered heterocyclic compounds containing highly coordinate main group elements. Most of them have distorted TBP structures with two atoms constructing the four-membered ring at the apical and equatorial positions. Elongation of the apical bond emerging from a three-centered four-electron bond seems to be a main factor for reducing the ring strain of the four-membered ring. One typical reaction for four-mem-



Scheme 24.

bered ring compounds is a Wittig-type cleavage, which was found in various types of compounds regardless of the kinds of the central atom and the substituents on the central atom. For pentacoordinate 1,2-oxasiletanides, we have demonstrated that they have both Peterson-type reactivity and homo-Brook rearrangement reactivity. Although we have succeeded in synthesis of the group 17 element analogue, the reactivity still remains to be explored. We have also disclosed two heteracyclobutanes containing a pentacoordinate phosphorus atom and two more heteroatoms, one of which has been considered as an intermediate of the aza-Wittig reaction. For three membered heterocyclic compounds, a few examples involving our two compounds have been reported to date. The chemistry of these compounds has just begun and further investigations are needed in order to understand systematically their reactivites.

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