Received: 29 September 2018 | Revised: 21 November 2018 | Accepted: 21 November 2018

DOI: 10.1002/hc.21473

SPECIAL ISSUE: A TRIBUTE TO PROFESSOR NAOMICHI FURUKAWA ON THE OCCASION OF HIS 82ND BIRTHDAY - BY INVITATION ONLY

WILEY Heteroatom Chemistry

Heteroatom effects toward isomerization of intermediates in Wittig reactions of non-stabilized phosphonium ylides bearing a phosphaheteratriptycene skeleton with benzaldehyde

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Funding information
Ministry of Education, Culture, Sports, Science, and Technology of Japan, Grant/Award Number: 16750041 and 18750037; Ogasawara Foundation for Oversea Visiting Researchers; Mikiya Foundation for Oversea Visiting Researchers; Kitasato University Research Grant for Young Researchers; Murata Science Foundation

Abstract

Isomerization of intermediates, *cis*- and *trans*-1,2-oxaphosphetanes, in Wittig reactions of non-stabilized phosphonium ylides bearing a phosphaheteratriptycene skeleton containing group 14 (PhSi, PhGe, PhSn, *n*-BuSn) and 15 (P, As, Sb, and Bi) elements with benzaldehyde (PhCHO) was investigated by variable-temperature (VT)^{31}P{^{1}H} NMR spectroscopy. The isomerization from the *cis*-1,2-oxaphosphetane to the *trans*-form occurred at lower temperatures as the row number of the same group elements increases. Wittig reactions under the same conditions gave the (*Z*)-olefin as a major product in the cases of period 3 elements (PhSi and P) and the (*E*)-olefin as a major product in the cases of elements from period 4 and below (PhGe, PhSn, *n*-BuSn, As, Sb, and Bi). The selectivity of olefin formation is considered to depend on the isomerization temperature of the intermediates, because each olefin must be obtained from the corresponding 1,2-oxaphosphetane. The VT-^{31}P{^{1}H} NMR spectra showed that the *cis*-1,2-oxaphosphetanes were the kinetic products in the first step of Wittig reactions and the *trans*-forms were the thermodynamically stable products formed by isomerization from the *cis*-forms via ring-opening and ring-closing reactions of phosphonium ylides with PhCHO. Density functional theory (DFT) calculations indicated that *cis*-1,2-oxaphosphetanes were less stable than the *trans*-forms by ~2 kcal/mol, supporting thermodynamically favorable isomerization from *cis*-forms to *trans*-forms, as observed by VT-^{31}P{^{1}H} NMR spectroscopy. Heteroatoms at the bridgehead position of the phosphaheteratriptycene skeleton significantly affected the isomerization temperature as well as the phosphorus-31 signals in the ^{31}P{^{1}H} NMR spectra, which were observed at lower field as row number of the same group element increases.

Dedicated to Professor Naomichi Furukawa on the occasion of his 82nd birthday.

Contract grant sponsor: Murata Science Foundation

Contract grant sponsor: Ministry of Education, Culture, Sports, Science, and Technology of Japan

Contract grant number: 16750041

Contract grant number: 18750037

Contract grant sponsor: Ogasawara Foundation for Oversea Visiting Researchers

Contract grant sponsor: Mikiya Foundation for Oversea Visiting Researchers

Contract grant sponsor: Kitasato University Research Grant for Young Researchers

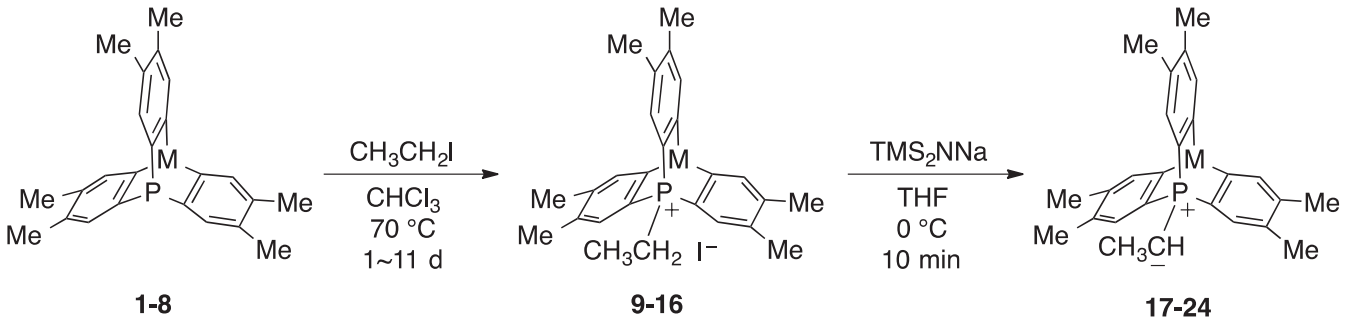
1 | INTRODUCTION

Numerous mechanistic studies on the Wittig reaction have indicated that the 1,2-oxaphosphetanes, which are regarded as a [2 + 2] cycloadduct constructed by a phosphonium ylide with a carbonyl compound, are detectable and isolatable intermediates.[1–4] ^{31}P NMR spectroscopy has been used as a powerful investigative tool to detect intermediates since Vedejs[5] and Maryanoff[3,6] observed signals due to 1,2-oxaphosphetanes in Wittig reactions of a non-stabilized triphenylphosphonium ylide with a carbonyl compound.[5–7] However, 1,2-oxaphosphetanes with π-conjugated substituents, such as phenyl and carbonyl groups, at the 3-position in the triphenylphosphine system have never been detected by ^{31}P NMR spectroscopy; these are regarded as intermediates in the reactions of a semi-stabilized phosphonium ylide or a stabilized phosphonium ylide with a carbonyl compound. These substituents at the neighboring position of phosphorus in the phosphonium ylides promote the decomposition of 1,2-oxaphosphetane due to its slightly polar transition state in the second step of the Wittig reaction.[8]

Since 1,2-oxaphosphetanes have a trigonal bipyramidal (TBP) structure, bidentate ligands that enable the formation of a five-membered ring stabilize such a TBP structure thermodynamically by occupying the apical and equatorial positions.[9] For example, Vedejs et al developed a novel dibenzophosphole system to stabilize the 1,2-oxaphosphetane with a vinyl group at the 3-position and observed its signal by ^{31}P NMR spectroscopy.[10,11] The Martin bidentate ligand has been used to stabilize highly coordinate heteroatom compounds.[12,13] Kawashima et al reported the isolation and crystal structure of the 1,2-oxaphosphetane with a methoxycarbonyl group at the 3-position bearing the Martin bidentate ligand.[14] They claimed that the compound recognized as a formal [2 + 2] cycloadduct of a stabilized phosphorus ylide and a carbonyl compound could be obtained as a stable compound and that the methoxycarbonyl group at the 3-position accelerated the olefin formation reaction. In the same bidentate ligand system, *O*-apical and *O*-equatorial 1,2-oxaphosphetanes, which have been predicted by theoretical calculations,[15] were evidenced by isolation of these intermediates and reported by Akiba et al for the first time.[16]

In contrast to the role of a bidentate ligand to stabilize highly coordinate 1,2-oxaphosphetanes, a tridentate ligand based on a phosphastibatriptycene skeleton did not show any stabilization of the intermediates, but resulted in the promotion of isomerization from the *cis*-1,2-oxaphosphetane to the *trans*-form in the Wittig reaction of a non-stabilized phosphonium ylide with PhCHO.[17–19] The Wittig reaction yielded the (*E*)-olefin as a major product, with the *cis*-1,2-oxaphosphetane being observed only in the initial step of this reaction, when monitored by variable-temperature (VT)^{31}P{^{1}H} NMR spectroscopy. This indicated that *cis*-1,2-oxaphosphetane had been isomerized to the *trans*-form, because (*Z*)- and (*E*)-olefins were produced from *cis*- and *trans*-1,2-oxaphosphetanes, respectively. This isomerization is known as the stereochemical drift in Wittig reactions of non-stabilized phosphonium ylides with a carbonyl compound, and shows the difference between the isomer ratio of the initial intermediates and that of the resulting olefins.[3,6,20,21] The stereochemical drift has been reported to depend on the substituent groups, such as phenyl and *n*-butyl groups, on the phosphorus of the 1,2-oxaphosphetane.[3,6,20] The phosphastibatriptycene system significantly affected the stereochemical drift unlike the tri-*n*-butylphosphine system, resulting in the selective formation of (*E*)-olefin in the Wittig reaction of non-stabilized phosphonium ylide with PhCHO.

We have been interested in heteroatom effects at the bridgehead position of the phosphaheteratriptycenes; these are the group 14 (PhSi, PhGe, PhSn, *n*-BuSn) and group 15 (P, As, Bi) element analogues of the phosphastibatriptycene.[22,23] In this paper, we report heteroatom effects on the isomerization from *cis*-1,2-oxaphosphetanes to the *trans*-forms in Wittig reactions of non-stabilized phosphonium ylides bearing the phosphaheteratriptycene skeleton with PhCHO. We also report the ^{31}P{^{1}H} NMR spectra of the related compounds based on the experimental and theoretical results.



SCHEME 1 Synthesis of ethylphosphonium iodides **9-16** and non-stabilized phosphonium ylides **17-24** bearing the phosphaheteratriptycene skeleton

TABLE 1 Phosphorus-31 chemical shifts (δ_P) of phosphorus compounds

M	Phosphaheteratriptycene[a]	Ethylphosphonium iodide[a]	Non-stabilized phosphonium ylide[b]	*cis*-1,2-Oxaphosphetane[c]	*trans*-1,2-Oxaphosphetane[d]	Phosphine oxide[a]
PhSi	**1** (−47.6)	**9** (−6.14)	**17** (−16.8)	**25a** (−81.3)	**25b** (−80.0)	**33** (-)
PhGe	**2** (−47.7)	**10** (−9.05)	**18** (−18.4)	**26a** (−82.8)	**26b** (−81.0)	**34** (1.55)
PhSn	**3** (−33.4)	**11** (−7.79)	**19** (−20.2)	**27a** (−76.2)	**27b** (−74.7)	**35** (1.99)
n-BuSn	**4** (−30.8)	**12** (−7.34)	**20** (−12.4)	**28a** (−75.6)	**28b** (−73.7)	**36** (3.61)
P	**5** (−46.1)	**13** (−2.56)	**21** (−13.6)	**29a** (−80.1)	**29b** (−78.2)	**37** (5.54)
As	**6** (−34.5)	**14** (1.32)	**22** (−7.57)	**30a** (−73.4)	**30b** (−71.3)	**38** (9.30)
Sb[17]	**7** (−10.1)	**15** (12.2)	**23** (6.63)	**31a** (−57.3)	**31b** (−55.2)	**39** (22.7)
Bi	**8** (12.5)	**16** (54.4)	**24** (45.5)	**32a** (−14.2)	**32b** (−12.8)	**40** (65.3)

[a]In $CDCl_3$ at room temperature.
[b]In THF at 0°C.
[c]In THF at −80°C.
[d]In THF at −20°C for **25b**, −50°C for **26b**, −50°C for **27b**, −60°C for **28b**, 0°C for **29b**, −20°C for **30b**, −40°C for **31b**, −60°C for **32b**.

2 | RESULTS AND DISCUSSION

2.1 | Ethylation of phosphaheteratriptycenes and generation of non-stabilized phosphonium ylides

Phosphaheteratriptycenes **1-8** containing group 14 and 15 elements, which were synthesized by the same method as phosphasilatriptycene[24] and phosphastibatriptycene **7**,[25,26] were reacted with ethyl iodide in $CHCl_3$ to give ethylphosphonium iodides **9-16** (Scheme 1). These ethylphosphonium iodides **9-16** were identified by (a) the phosphorus-31 signals that were detected at lower field than those of phosphaheteratriptycenes **1-8**, (b) proton signals of the CH_3CH_2 group observed in the alkyl region, and (c) their H–H and P–H couplings. Non-stabilized phosphonium ylides **17-24** bearing the phosphaheteratriptycene skeleton were generated in a yellow THF solution by the deprotonation of ethylphosphonium iodides **9-16** with $(TMS)_2NNa$ at 0°C (Scheme 1). Non-stabilized phosphonium ylides **17-24** generated in THF were examined in situ by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy. Unfortunately, the characteristic ylidic proton signals could not be observed due to the THF solvent signals, which were much larger than those of the desired phosphonium ylides **17-24**. However, the phosphorus-31 signals in the $^{31}P\{^1H\}$ NMR spectra of **17-24** in THF were at notably higher field than those of **9-16** in $CDCl_3$, whose chemical shifts were compared in different solvents because of their solubility in THF (Scheme 1, Table 1, and Figure 1). Wittig reactions were conducted by the addition of PhCHO to the yellow solutions below −90°C. The color change from yellow to colorless indicated that the Wittig reactions started at −90°C and the formation of intermediates also proceeded at the same temperature (Scheme 2, Table 1, and Figure 1).

2.2 | P-Si and P-Sn coupling constants of phosphasilatriptycenes, *Sn*-phenylphosphastannatriptycenes, and *Sn*-*n*-butylphosphastannatriptycenes

The P-Si coupling constant of ethyl phosphonium salt **9** (56.6 Hz), which depended on the oxidation state of phosphorus, was observed to be ~8 times larger number than that of phosphasilatriptycene **1** (7.15 Hz) in ^{29}Si NMR spectra. The P-Sn coupling constants of **11** and **12** (302.6 and 237.9 Hz, respectively) were ~5 times larger than those of **3** and **4** (65.0 and 48.8 Hz, respectively) in ^{119}Sn NMR spectra. Similarly, the coupling constants of **11** and **12** were 302.4 and 237.9 Hz, respectively, and those of **3** and **4** were 64.0 and 50.0 Hz, respectively, in the ^{31}P NMR spectra, indicating the presence of oxidized phosphorus atoms in these compounds. Non-stabilized phosphonium ylide **20** and *trans*-1,2-oxaphosphetane **28b** in the ^{31}P NMR

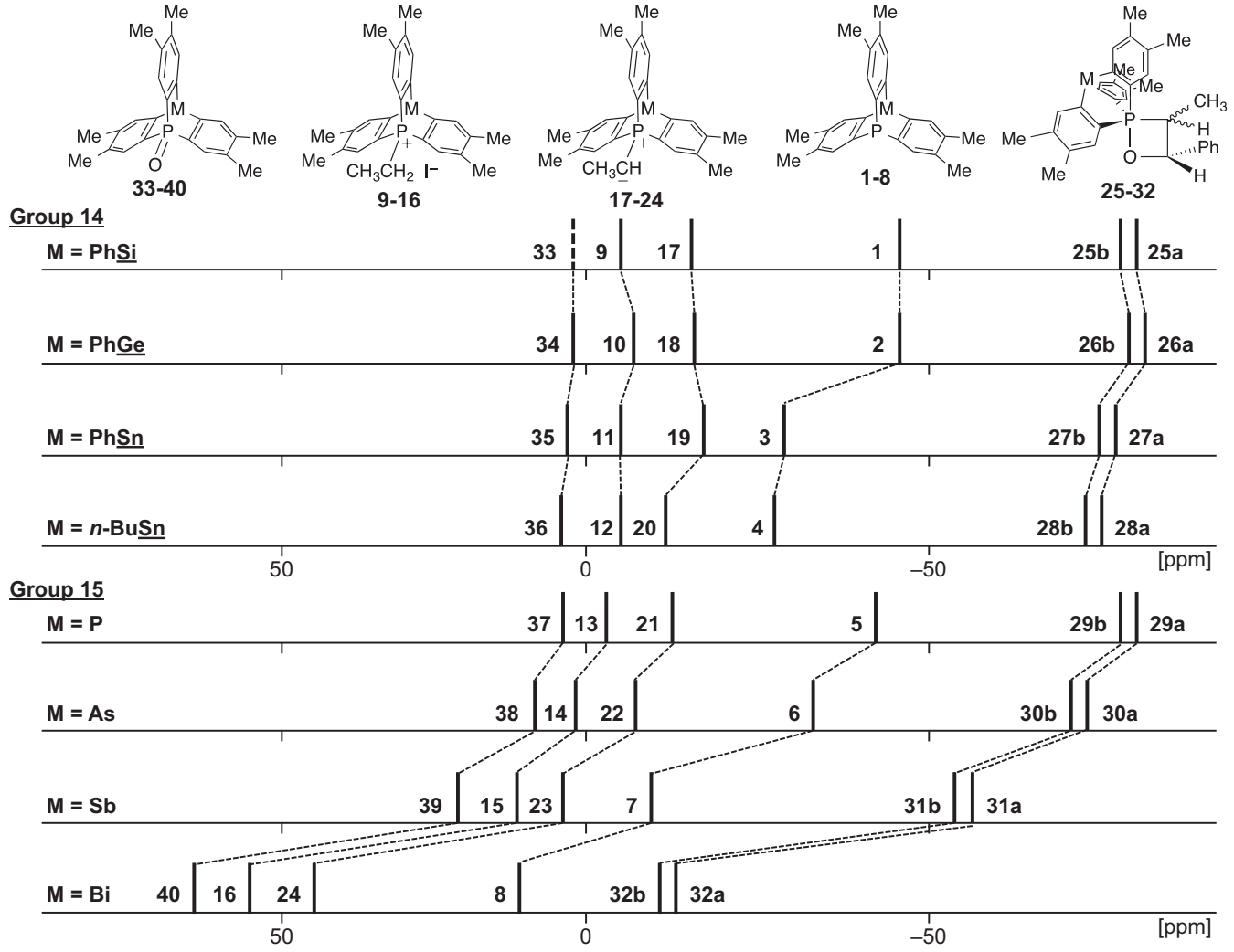
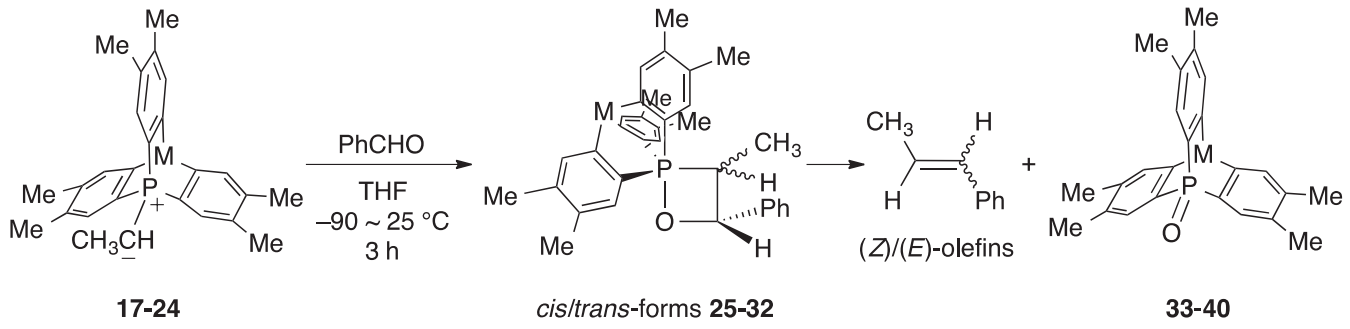


FIGURE 1 Systematic comparison of the ^{31}P NMR chemical shifts of phosphorus compounds



SCHEME 2 Wittig reactions of non-stabilized phosphonium ylides **17-24** with PhCHO

spectra had P-Sn coupling constants of 237.2 and 236.7 Hz, respectively, similar to that of ethylphosphonium salt **12**. However, the P–Sn coupling constant of phosphine oxide **36** was 267.0 Hz, which was somewhat larger than that of **12**, **20**, and **28b**. The P-Sn coupling constants were almost the same when the oxidation state and substituents on the phosphorus atom were the same. However, phenyl derivatives **3** and **11** showed larger P-Sn coupling constants than the *n*-butyl derivatives **4** and **12**, demonstrating the substituent effect on the tin atom. The results indicated that substituents on the heteroatom at the bridgehead position affected the phosphorus atom and its oxidation state (in other words, the difference in the s-character of the bond), and directly induced the large change from the pyramidal structure of

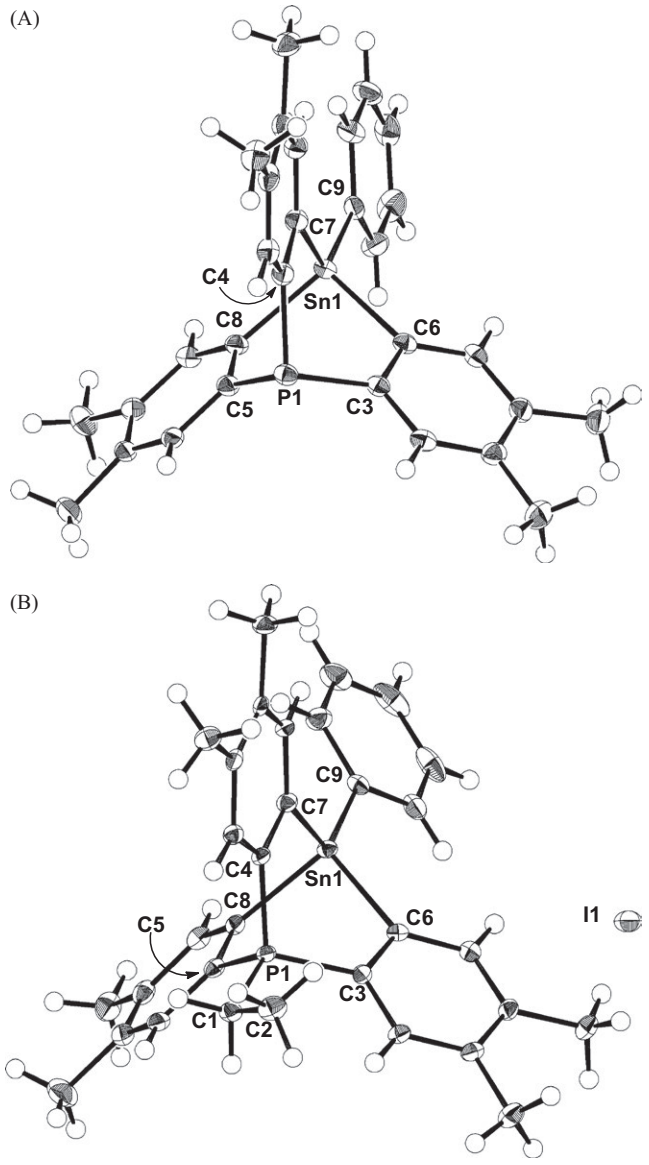


FIGURE 2 Crystal structure of phenylphosphatriptycenes **3** and **11**, selected bond lengths (Å) of **3** are P1–C3; 1.855(2), P1–C4; 1.860(2), P1–C5; 1.855(2), Sn1–C6; 2.134(2), Sn1–C7; 2.131(2), Sn1–C8; 2.134(2), Sn1-C9; 2.116(2), P1···Sn1; 3.293, selected bond angles (°) of **3** are C3–P1–C4; 101.55(7), C3–P1–C5; 100.60(7), C4–P1–C5; 102.04(7), C6–Sn1–C7; 96.95(6), C6–Sn1–C8; 97.14(6), C6–Sn1–C9; 117.13(6), C7–Sn1–C8; 97.54(6), C7–Sn1–C9; 125.53(6), C8–Sn1–C9; 119.16(6), selected bond lengths (Å) of **11** are P1–C1; 1.795(3), P1–C3; 1.811(3), P1–C4; 1.809(3), P1–C5; 1.807(3), Sn1–C6; 2.154(3), Sn1–C7; 2.150(3), Sn1–C8; 2.161(3), Sn1–C9; 2.114(3), P1···Sn1; 3.180, selected bond angles (°) of **11** are C1–P1–C3; 112.59(13), C1–P1–C4; 111.67(13), C1–P1–C5; 110.63(13), C3–P1–C4; 107.62(12), C3–P1–C5; 105.54(12), C4–P1–C5; 108.52(12), C6–Sn1–C7; 123.86(10), C6–Sn1–C8; 94.24(10), C6–Sn1–C9; 96.29(10), C7–Sn1–C8; 96.58(10), C7–Sn1–C9; 123.70(10), C8–Sn1–C9; 115.93(10)

phosphines **3** and **4** to tetrahedral or trigonal bipyramidal structures of the phosphonium salts **11** and **12**, phosphonium ylide **20**, and *trans*-1,2-oxaphosphetane **28b**.

2.3 | X-ray crystallographic analysis of *Sn*-phenylphosphastannatriptycenes

In order to investigate the structure around the phosphorus atom, X-ray analysis was carried out on the single crystals of phenylphosphastannatriptycenes **3** and **11** obtained from $CHCl_3$-acetone and CH_2Cl_2-benzene, respectively (Figure 2 and Table 3). The results showed that the pyramidal geometry around phosphorus atom in Figure 2A changed to a tetrahedral geometry upon ethylation of *Sn*-phenylphosphastannatriptycene **3**, as shown in Figure 2B. That is, the P–C bonds of **11** are somewhat shorter than those of **3**, whereas the C–P–C angles of **11** are somewhat larger than those of **11**. On the other hand, *Sn*-phenylphosphastannatriptycene **3** has a tetrahedral structure around tin atom with the Sn–C bonds and C–Sn–C angles described in Figure 2A. These are similar to those of the ethylphosphonium derivative **11** having Sn–C bonds and C–Sn–C angles, as shown in Figure 2B. These bond lengths and angles around the phosphorus and tin atoms affected the spatial distances between phosphorus and tin, P···Sn (3.293 and 3.180 Å), as well as in the reported structures of phosphastibatriptycenes **7** and **15** having P···Sb distances, 3.482 and 3.349 Å.[17]

2.4 | Wittig reactions of non-stabilized phosphonium ylides with PhCHO

Wittig reactions of non-stabilized phosphonium ylides **17-24** with PhCHO at −90°C gave (*Z*)- and (*E*)-olefins through 1,2-oxaphosphetanes **25-32** as intermediates, which were observed at temperatures between −90°C and 25°C by VT-$^{31}P\{^1H\}$ NMR spectroscopy (Scheme 2). Wittig reactions at −90°C provided the (*Z*)-olefin as a major product in the cases of period 3 elements (Ph<u>Si</u> and P) and (*E*)-olefin as a major product in the cases of elements from period 4 and below (Ph<u>Ge</u>, Ph<u>Sn</u>, *n*-Bu<u>Sn</u>, As, Sb, and Bi) in moderate yields together with phosphine oxides **33-40** (Scheme 2 and Table 2). The selectivity in Wittig reactions at 0°C agreed with that at −90°C except for that of the ylide bearing the diphosphatriptycene skeleton, although an increase and decrease in the selectivity were observed. The presence of a particular heteroatom resulted in the selective formation of (*E*)-olefin for the period 4 and below elements of both groups 14 and 15 similar to that reported for the antimony system.[17]

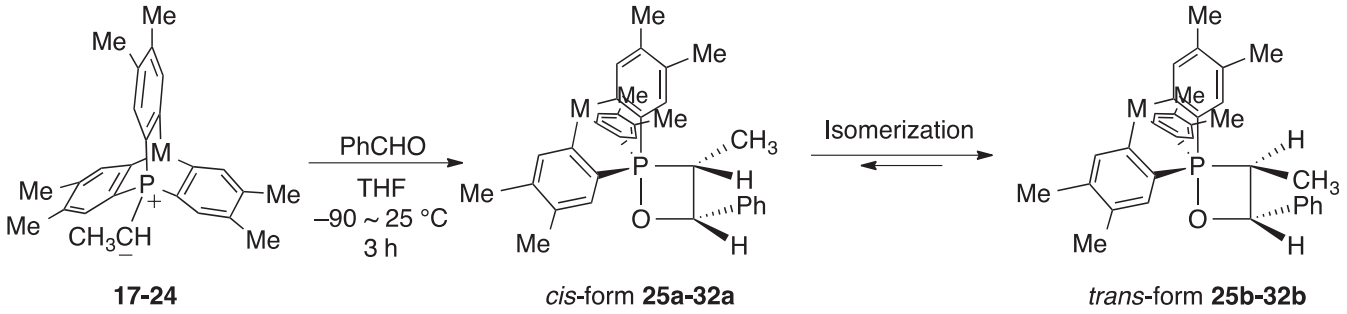
2.5 | Observation of intermediates by VT-$^{31}P\{^1H\}$ NMR spectroscopy

These (*E*)-selective Wittig reactions were induced by the stereochemical drift caused by the isomerization from *cis*-1,2-oxaphosphetanes **25a-32a** to the *trans*-forms **25b-32b**, as shown in Scheme 3. The isomerization temperatures of the

TABLE 2 (*Z*)/(*E*)-Ratios of produced olefins and yields (%) in Wittig reactions, isomerization temperature (°C), and electronegativity

Entry	M	(*Z*)/(*E*) ratio[a,b] (Yield [%][a])	(*Z*)/(*E*) ratio[a,c] (Yield [%][a])	Isomerization temperature[d]	Electronegativity[e,f]
1	PhSi	62 : 38 (38)	87 : 13 (47)	−20	1.74
2	PhGe	17 : 83 (72)	22 : 78 (55)	−50	2.02
3	PhSn	21 : 79 (34)	12 : 88 (55)	−50	1.82
4	*n*-BuSn	26 : 74 (45)	11 : 89 (47)	−60	1.82
5	P	51 : 49 (15)	48 : 52 (57)	0	2.06
6	As	35 : 65 (32)	36 : 64 (50)	−20	2.20
7	Sb[17]	13 : 87 (87)	20 : 80 (70)	−40	1.82
8	Bi	26 : 74 (42)	25 : 75 (58)	−60	1.67

[a]Integration ratio at 25°C in ^{1}H NMR spectra estimation yield toward the inner standard, $Ph_2C{=}CH_2$.
[b]Wittig reactions at −90°C.
[c]Wittig reactions at 0°C.
[d]Temperature as *trans*-form increased in VT-^{31}P{^{1}H} NMR spectra.
[e]Electronegativity (Allred-Rochow).[27]
[f]Carbon; 2.50.[27]



SCHEME 3 Observation of isomerization from *cis*-1,2-oxaphosphetanes **25a-32a** to *trans*-form **25b-32b** by VT-^{31}P{^{1}H} NMR spectroscopy

1,2-oxaphosphetanes **25-32** bearing the phosphaheteratriptycene skeleton containing group 14 and 15 elements were studied by VT-^{31}P{^{1}H} NMR spectroscopy (Figure 3). The temperature decreased as the row number of the same group elements increases, that is, −20°C for **25**, −50°C for **26**, −50°C for **27**, and −60°C for **28** in the cases of group 14 elements and 0°C for **29**, −20°C for **30**, −40°C for **31**, and −60°C for **32** in the cases of group 15 elements (Table 2). In the Sn system, substituent effect of the phenyl and *n*-butyl groups was observed by the VT-^{31}P{^{1}H} NMR measurement, wherein the *n*-butyl group on Sn promoted isomerization more effectively than the phenyl group. The observed isomerization temperature affected the selectivity of the olefin in Wittig reactions of non-stabilized phosphonium ylides **17-24** with PhCHO. The dependence of the accelerated isomerization of intermediates on the heteroatoms at another bridgehead position of the phosphaheteratriptycene skeleton was in a good agreement with the result of (*E*)-selective olefin formation in Wittig reactions. The heteroatom effect was comparable with the tendency of electronegativity, inducing M(δ^+)–C(δ^-) polarization in the phosphaheteratriptycene skeleton, which led to the retro-[2 + 2] cycloaddition reaction of *cis*-1,2-oxaphosphetane.

VT-^{31}P{^{1}H} NMR spectroscopic studies of all the reactions showed that *cis*-1,2-oxaphosphetanes **25a-32a** were almost the exclusive kinetic products at −90°C. The highly selective *cis*-1,2-oxaphosphetane formation was observed in these phosphaheteratriptycene systems without exception, which was quite different from the results of the triphenylphosphine and tri-*n*-butylphosphine systems.[4,5,17] The *cis*-1,2-oxaphosphetanes produced were isomerized to the thermodynamically stable *trans*-forms, which were followed by the decomposition of the 1,2-oxaphosphetane ring to give the olefin and phosphine oxides **33-40**. Therefore, the phosphaheteratriptycene skeletons generated *cis*-1,2-oxaphosphetanes **25a-32a** as initial major products in the Wittig reactions.

The intermediates bearing a phosphaheteratriptycene skeleton in the Wittig reactions, *cis*- and *trans*-1,2-oxaphosphetanes **25-32**, were observed as a sharp signal in the VT-^{31}P{^{1}H} NMR spectra except for *cis*-1,2-oxaphosphetanes **27a** and **28a** bearing *Sn*-phenylphosphastannatriptycene and *Sn*-*n*-butylphosphastannatriptycene skeletons, respectively. These oxaphosphetanes were observed as broad signals (Figure 3). In the phosphastibatriptycene system, such broad

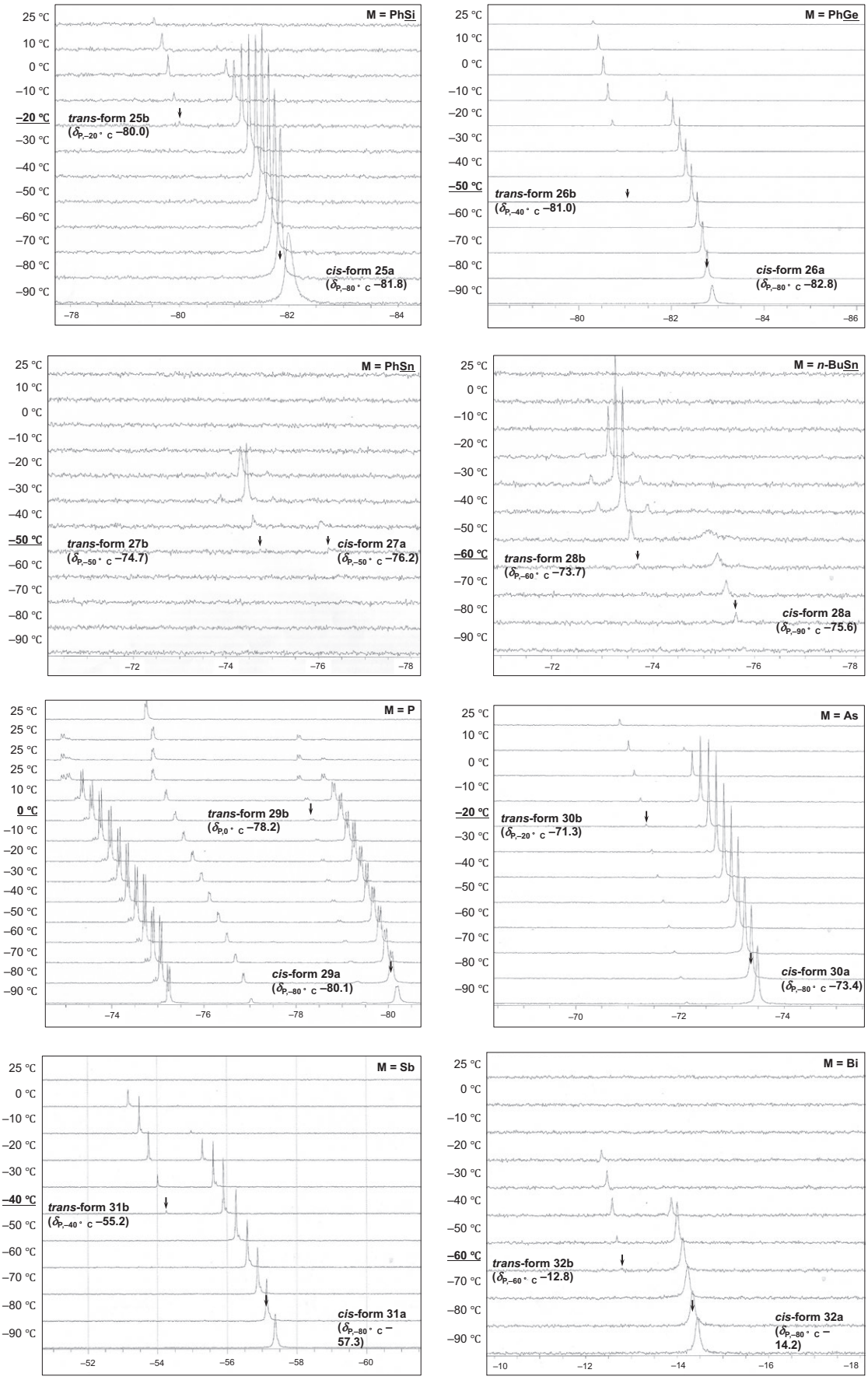


FIGURE 3 VT-$^{31}P\{^{1}H\}$ NMR spectra of *cis*- and *trans*-1,2-oxaphosphetanes **25-32**

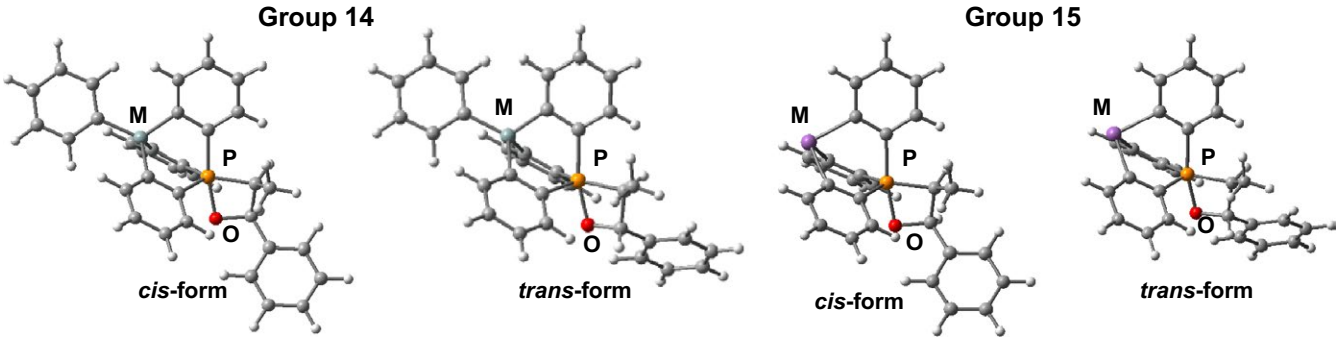


FIGURE 4 Optimized structures of 1,2-oxaphosphetanes bearing the phosphaheteratriptycene skeleton containing group 14 and 15 elements

signals of both *trans*- and *cis*-1,2-oxaphosphetanes were observed only at −40°C and −90°C, respectively, in the presence of lithium ions by VT-$^{31}P\{^{1}H\}$ NMR spectroscopy without any other intermediates.[17] On the other hand, a broad signal at −75.6 ppm was assigned to *cis*-1,2-oxaphosphetane **28a** in the *n*-butylphosphastannatriptycene systems that was formed in the Wittig reaction of non-stabilized phosphonium ylide **20** with PhCHO under salt-free condition at −90°C. This was related to another broad signal at −2.72 ppm in the VT-$^{31}P\{^{1}H\}$ NMR spectra, which could be attributed to the reversible change in an equilibrium at temperature between −40°C and −90°C. These results suggest that *cis*-1,2-oxaphosphetane **28a** was in equilibrium with another species, such as an *anti*-betaine intermediate.

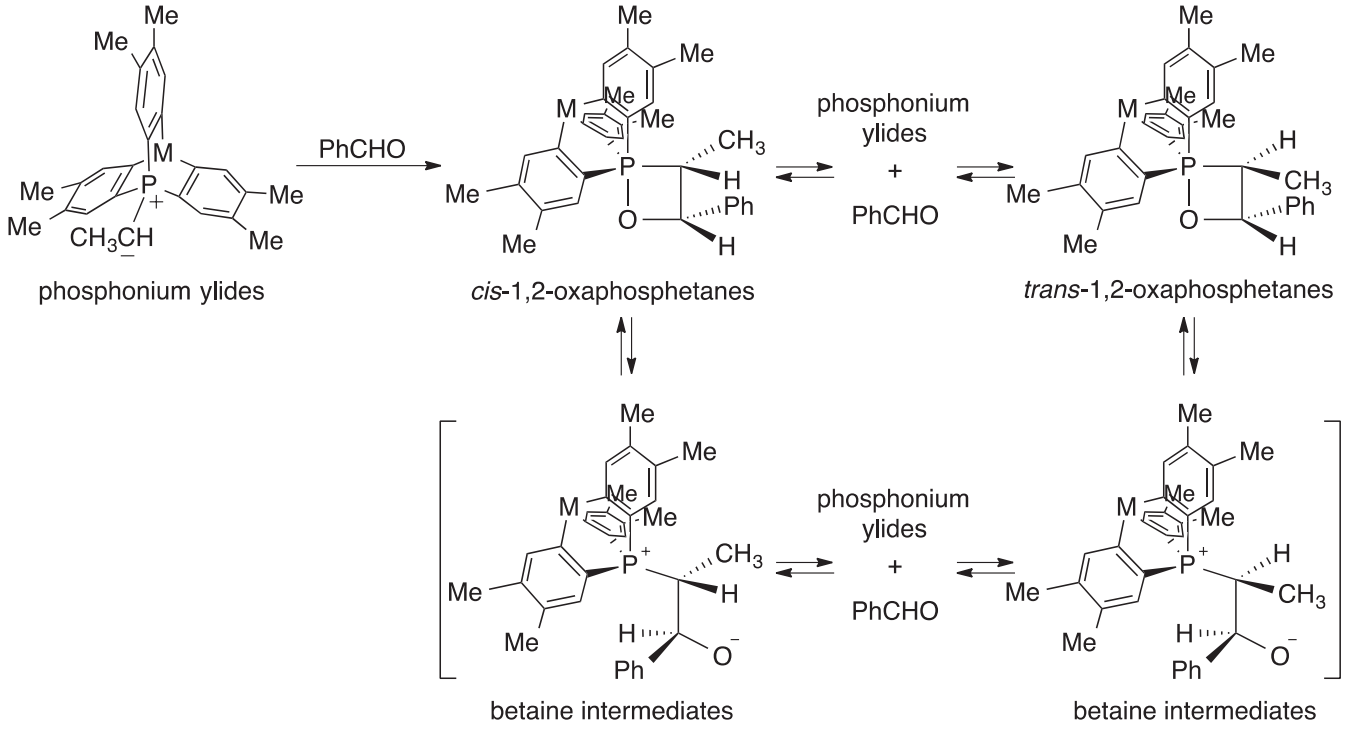
2.6 | DFT calculations to obtain free energies and phosphorus-31 chemical shifts of 1,2-oxaphosphetanes bearing the phosphaheteratriptycene skeleton

Density functional theory (DFT) calculations were carried out for the 1,2-oxaphosphetanes bearing the phosphaheteratriptycene skeleton containing group 14 and 15 elements in order to estimate the optimized structures, free energies at 298 K, and phosphorus-31 NMR chemical shifts (Figure 4 and Table 4). The optimized structure was confirmed by frequency analysis, which showed the global minimum structure due to zero imaginary frequency.[28] In all 1,2-oxaphosphetanes, the *trans*-forms are ~2 kcal/mol more stable than the *cis*-forms because of the absence of steric hindrance between the methyl and phenyl groups at 3- and 4-positions. This is in good agreement with the results of VT-$^{31}P\{^{1}H\}$ NMR spectroscopy. Phosphorus-31 signals reveal that *cis*- and *trans*-1,2-oxaphosphetanes were the kinetic and thermodynamic products, respectively. This is because, for all the cases, the signals due to the *cis*-forms were observed much earlier than those due to the *trans*-forms. Signals were observed at the different temperatures depending on the heteroatom at the bridgehead position of the phosphaheteratriptycene skeleton. M···P distances were found to be in the range of 3.15-3.65 Å, which are much shorter than the sum of van der Waals radii (2.00 Å for Si, 1.90 Å for P, 2.00 Å for As, 2.20 Å for Sb, and 2.40 Å for Bi).[27] This suggests the possibility of interactions between the M and phosphorus atoms.

Phosphorus-31 chemical shifts of *cis*- and *trans*-1,2-oxaphosphetanes bearing the phosphaheteratriptycene skeleton were observed within 2 ppm of each other, whereas those of other phosphorus compounds were observed over a wider chemical shift, depending on the heteroatom at the bridgehead position of the phosphaheteratriptycene. Phosphorus-31 chemical shifts of 1,2-oxaphosphetanes with different heteroatoms were estimated by the GIAO method with an all electron basis set (DZP).[29–32] The calculated phosphorus-31 NMR chemical shifts did not agree accurately with the measured values, but the tendency of the signal to appear at lower field as the row number increases was in good agreement with the observed NMR results. The results showed that the phosphorus-31 chemical shifts depended on the heteroatom at the bridgehead position of the phosphaheteratriptycene. On the other hand, the temperature of isomerization from *cis*-1,2-oxaphosphetanes to their *trans*-forms seems to depend on the readiness of the ring-opening reaction, because the isomerization is considered to occur via ring-opening and ring-closing reactions of phosphonium ylides with PhCHO. In an equilibrium between the 1,2-oxaphosphetanes and phosphonium ylides-PhCHO, the equilibrium inclines more toward the right side because of the increase in stability of the phosphonium ylides.

2.7 | Mechanism of isomerization from *cis*-1,2-oxaphosphetane to *trans*-form in the Wittig reaction

We have considered the mechanism of Wittig reactions of non-stabilized phosphonium ylides with PhCHO based on our previous results using the stibine derivative as shown in Scheme 4. The reactions gave (*Z*)- and (*E*)-olefins, whose ratios are highly dependent on the potential of the substituents on the phosphorus atom, based on how much they can stabilize the phosphorus ylide. In the phosphaheteratriptycene



SCHEME 4 Plausible mechanism for Wittig reactions and isomerization from *cis*-1,2-oxaphosphetanes to *trans*-forms

system, the heteroatom at the bridgehead position induced the stabilization of the non-stabilized phosphonium ylide; similar results were observed for the tri-*n*-butylphosphine system as well.[3,6,20] The phosphonium ylides can be stabilized by the negative charge on the carbon emerging from the M(δ^+)–C(δ^-) bond polarization, and its extent is dependent on the electronegativity of the heteroatom; that is, the ylide is more stabilized as the electronegativity of the heteroatoms decreases. Indeed, the phosphaheteratriptycene skeleton works as a tridentate ligand and electron-donating aryl groups toward phosphorus atoms, which causes an upfield shift of phosphorus atom (δ_P −47.6 for **1**, −47.7 for **2**, −33.4 for **3**, −30.8 for **4**, −46.1 for **5**, −34.5 for **6**, and −10.1 for **7**) toward the triphenylphosphine system (δ_P −5.39). This was similar to that observed for the *n*-butyl group in the tri-*n*-butylphosphine system (δ_P −30.6), although phosphabismatriptycene **8** was observed at 12.5 ppm (Table 1). As a result, isomerization from the *cis*-1,2-oxaphosphetanes to the *trans*-forms occurs easily via phosphaheteratriptycene, resulting in (*E*)-selective olefin formation.

The isomerization is derived from the equilibrium between 1,2-oxaphosphetane and the non-stabilized phosphonium ylide-PhCHO rather than the inversion at the α-carbon of the Schlosser type intermediate.[33] This was confirmed based on the results of the crossover experiments of β-hydroxyalkylphosphonium salt bearing the phosphastibatriptycene skeleton in the presence of *p*-chlorobenzaldehyde.[17] The investigation showed both *cis*-1,2-oxaphosphetanes (δ_P −56.5 and −56.6) composed of non-stabilized phosphonium ylide with PhCHO and *p*-chlorobenzaldehyde at −40°C at the same time, indicating the formation of the cross product. Therefore, other phosphaheteratriptycenes are expected to behave similar to the phosphastibatriptycene system. Since the cross product was formed at the temperature of the isomerization, the equilibrium of each phosphaheteratriptycene is considered to occur at the observed temperature of isomerization.

Although the equilibrium was not revealed to occur via betaine intermediates or direct retro-[2 + 2] cycloaddition reaction in this study, *cis*-1,2-oxaphosphetane **28a** bearing the phosphastannatriptycene skeleton was observed as a broad signal at from −90°C to −50°C in the VT-$^{31}P\{^1H\}$ NMR spectra. Also, the signal was related to another broad signal at a higher filed in the VT-$^{31}P\{^1H\}$ NMR spectra, which was attributed a reversible change. Another species, such as an *anti*-betaine intermediate (Scheme 4), could be considered in the equilibrium based on the experimental results, although *cis*-1,2-oxaphosphetanes bearing the phosphaheteratriptycene skeleton (observed as a sharp signal) might proceed via a different pathway such as the retro-[2 + 2] cycloaddition reaction.

3 | CONCLUSION

In this paper, the heteroatom effect of the phosphaheteratriptycene skeleton toward the isomerization from the *cis*-1,2-oxaphosphetanes to their *trans*-forms was described based on the results obtained from VT-$^{31}P\{^1H\}$ NMR spectroscopy,

and supported by DFT calculations. The selectivity of (*Z*)/(*E*)-olefins in the reaction was attributed to the readiness of the isomerization of the intermediates derived from the equilibrium between the 1,2-oxaphosphetanes and the non-stabilized phosphonium ylides-PhCHO. The heteroatom effect also induced the upfield shift of phosphorus nuclei in the phosphaheteratriptycene, as compared to that of the triphenylphosphine system (except in the case of phosphabismatriptycene skeleton) because of the $M(\delta^+)$–$C(\delta^-)$ polarization arising from electronegativity and low-field shift of phosphorus-31 signals of the phosphaheteratriptycene skeleton as the row number of the same group element increases. In the phosphastannatriptycene system, it was shown that *cis*-1,2-oxaphosphetane **28a** was probably in equilibrium with another intermediate, such as a betaine, as concluded from the broad signal in the VT-$^{31}P\{^1H\}$ NMR spectra. Thus, the interesting phenomena observed in the Wittig reaction of non-stabilized phosphonium ylides bearing the phosphaheteratriptycene skeleton with PhCHO prompt us to further investigate their detailed mechanism.

4 | EXPERIMENTAL SECTION

4.1 | General

^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra were recorded by Bruker Advance-III or Bruker Advance-II 600 (600 MHz for ^1H, 151 MHz for ^{13}C, 243 MHz for ^{31}P, 119 MHz for ^{29}Si and 224 MHz for ^{119}Sn) spectrometer at room temperature as the inner standards of TMS (δ_H 0.00), acetone-d_6 (δ_H 2.06), $CDCl_3$ (δ_C 77.0), H_3PO_4 (δ_P 0.00), TMS (δ_{Si} 0.00), and *n*-Bu_4Sn (δ_{Sn} 0.00). Melting points were measured by Yanaco micro-melting point apparatus. ESI-MS spectroscopy was conducted by Exactive Plus of Thermo Fisher Co. X-ray crystallographic analysis was performed by SMART APEX II of Bruker AXS Co. Reagents and solvents for synthesis were purchased from Nacalai Tesque, Kanto Chemical Co., INC., Wako Pure Chemical Industries, Ltd., Sigma-Aldrich Co. LLC., Cambridge Isotope Laboratories, Alfa Aesar, and MERCK. 1.58-1.60 M $(TMS)_2NNa$ in THF made in KANTO was used for the generation of non-stabilized phosphonium ylides. Dried THF and Et_2O were used from the solvent cans of KANTO without any further purification.

4.2 | Synthesis of 2,3,6,7,14,15-hexamethyl-9-phospha-10-heteratriptycenes

4.2.1 | General process

Under nitrogen, to a THF (100 mL) solution of tris(2-bromo-4,5-dimethylphenyl)phosphine (1.00 g, 1.72 mmol) in 200-mL three-necked round flask with a −100 ~ 50°C thermometer and a septa was added 1.60 M pentane solution of *t*-BuLi (4.2 mL, 6.72 mmol, 3.9 equivalent toward the starting triarylphosphine) from a 5 mL syringe at −90°C to −85°C for 5 min, to give deep yellow clear solution through green solution. The reaction mixture was stirred at −90°C for 30 min. A THF (15 mL) solution of MCl_3 (M = PhSi, PhGe, PhSn, *n*-BuSn, P, As, Sb, and Bi) was added to the reaction mixture at −90°C to −85°C for 10 min by a Teflon transfer tube from 50-mL two-neck round-bottom flask, and the mixture was stirred for 1 hour at the same temperature. Evaporation of the solvent, THF, was performed before treatment of the mixture with aqueous NH_4Cl (40 mL) and the extraction with $CHCl_3$ (40 mL × 3). The organic layer was washed with water (40 mL) and aqueous NaCl (40 mL) and dried over $MgSO_4$. The treated organic solution was evaporated to give a yellow solid, and then, the solid was filtrated with AcOEt-hexane in a ratio of 1:1. The filtrate was evaporated after removing white polymer, and the residue was washed with acetone to give phosphaheteratriptycenes **1-8** as a white solid.

2,3,6,7,14,15-Hexamethyl-10-Phenyl-9-phospha-10-silatriptycene 1: White solid [m.p 269.5~272.3°C], ^1H NMR (600 MHz, $CDCl_3$) δ = 2.15 (9H, s), 2.19 (9H, s), 7.47 (3H, s), 7.69-7.71 (6H, m), 8.26-8.27 (2H, m), $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ = 19.51 (p), 19.52 (p), 128.2 (q), 128.7 (t), 130.7 (t), 134.4 (t), 135.91 (q), 136.1 (q, $^2J_{CP}$ = 46.5 Hz), 136.2 (t, $^3J_{CP}$ = 15.1 Hz), 136.4 (t), 139.5 (q, $^4J_{CP}$ = 2.11 Hz), 144.7 (q, $^3J_{CP}$ = 6.49 Hz), $^{31}P\{^1H\}$ NMR (243 MHz, $CDCl_3$) δ = −47.7(s), $^{29}Si\{^1H\}$ NMR (119 MHz, $CDCl_3$) δ = −38.9 (d, $^3J_{SiP}$ = 7.15 Hz), ESI-MS [CH_3CN]: Found: *m/z* 449.1842, Calcd for $C_{30}H_{29}PSi$+H: 449.1849.

2,3,6,7,14,15-Hexamethyl-10-phenyl-9-phospha-10-germatriptycene 2: White solid [m.p 295.8~298.3°C], ^1H NMR (600 MHz, $CDCl_3$) δ = 2.16 (9H, s), 2.19 (9H, s), 7.47 (3H, s), 7.65-7.71 (3H, m), 7.73 (3H, d, $^3J_{PH}$ = 12.0 Hz), 8.12-8.14 (2H, m), $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ = 19.48 (p), 129.1 (t), 130.1 (t), 130.4 (q), 133.5 (t), 136.0 (t), 136.0 (q), 136.1 (q, $^1J_{PC}$ = 38.0 Hz), 136.7 (t, $^2J_{PC}$ = 49.7 Hz), 141.4 (q, $^3J_{PC}$ = 6.79 Hz), 142.6 (q, $^4J_{PC}$ = 1.66 Hz), $^{31}P\{^1H\}$ NMR (243 MHz, $CDCl_3$) δ = −47.7 (s), ESI-MS [CH_3CN]: Found: *m/z* 495.1287, Calcd for $C_{30}H_{29}PGe$+H: 495.1291.

2,3,6,7,14,15-Hexamethyl-10-phenyl-9-phospha-10-stannatriptycene 3: White solid [m.p 305.1~307.9°C], ^1H NMR (600 MHz, $CDCl_3$) δ = 2.17 (9H, s, $^4J_{SnH}$ = 116.4 Hz), 2.19 (9H, s, $^5J_{SnH}$ = 109.8 Hz), 7.52 (3H, s, $^3J_{SnH}$ = 43.8 Hz), 7.58-7.61 (1H, m), 7.64-7.66 (2H, m), 7.81 (3H, d, $^3J_{PH}$ = 13.8 Hz, $^4J_{SnH}$ = 18.0 Hz), 7.98-8.00 (2H, m, $^3J_{SnH}$ = 54.6 Hz), $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ = 19.3 (p), 19.5 (p), 129.5 (t, $^2J_{SnC}$ = 59.5 Hz), 130.2 (t, $^4J_{SnC}$ = 13.0 Hz), 132.9 (q), 136.3 (q), 136.4 (q), 136.4 (t, $^3J_{PC}$ = 16.6 Hz, $^2J_{SnC}$ = 9.66 Hz), 137.9 (t, $^3J_{PC}$ = 53.0 Hz, $^3J_{SnC}$ = 16.9 Hz), 138.1 (t, $^3J_{SnC}$ = 39.1 Hz), 142.2 (q, $^4J_{CP}$ = 8.60 Hz), 145.2 (q), $^{31}P\{^1H\}$ NMR (243 MHz, $CDCl_3$) δ = −33.4 (t, $^3J_{PSn}$ = 64 Hz), $^{119}Sn\{^1H\}$NMR (224 MHz, $CDCl_3$) δ = −256 (d, $^3J_{PSn}$ = 65 Hz), ESI-MS [CH_3CN]: Found: *m/z* 541.1098, Calcd for $C_{30}H_{29}PSn$+H : 541.1102.

10-*n*-Butyl-2,3,6,7,14,15-hexamethyl-9-phospha-10-stannatriptycene 4: colorless oil, ^{1}H NMR (600 MHz, $CDCl_3$) δ = 1.11 (3H, t, $^{3}J_{HH}$ = 7.2 Hz), 1.70-1.74 (2H, m), 2.06-2.14 (2H, m), 2.19-2.31 (2H, m), 2.16 (9H, s), 2.17 (9H, s), 7.44 (3H, s, $^{3}J_{SnH}$ = 41.4 Hz), 7.78 (3H, d, $^{3}J_{PH}$ = 13.2 Hz, $^{4}J_{SnH}$ = 14.4 Hz), ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ = 8.54 (s, $^{2}J_{SnC}$ = 428.1 Hz), 13.80 (p, $^{5}J_{SnC}$ = 12.9 Hz), 19.37 (p), 19.43 (p), 27.62 (s, $^{3}J_{SnC}$ = 55.7 Hz), 29.19 (s, $^{4}J_{SnC}$ = 29.4 Hz), 136.05 (q, $^{1}J_{PC}$ = 21.8 Hz, $^{2}J_{SnC}$ = 8.22 Hz), 136.09 (q, $^{4}J_{PC}$ = 7.28 Hz, $^{3}J_{SnC}$ = 8.22 Hz), 136.5 (t, $^{3}J_{PC}$ = 1.66 Hz, $^{2}J_{SnC}$ = 42.6 Hz), 137.7 (t, $^{2}J_{PC}$ = 53.0 Hz, $^{3}J_{SnC}$ = 29.9 Hz), 142.2 (q, $^{3}J_{PC}$ = 7.55 Hz, $^{4}J_{SnC}$ = 10.9 Hz), 146.2 (q, $^{1}J_{SnC}$ = 452.0 Hz), ^{31}P{^{1}H} NMR (243 MHz, $CDCl_3$) δ = −30.8 (t, $^{3}J_{PSn}$ = 50.0 Hz), ^{119}Sn{^{1}H}NMR (224 MHz, $CDCl_3$) δ = −217.5 (d, $^{3}J_{PSn}$ = 48.8 Hz), ESI-MS [CH_3CN]: Found: *m/z* 521.1417, Calcd for $C_{28}H_{34}PSn$: 521.1415.

2,3,6,7,14,15-hexamethyl-9,10-diphosphatriptycene 5: White solid [m.p. 340.0~343.0°C, lit[25] >300°C], ^{1}H NMR (600 MHz, $CDCl_3$) δ = 2.18 (18H, s), 7.66-7.70 (6H, m), ^{31}P{^{1}H} NMR (243 MHz, $CDCl_3$) δ = −45.3 (s), ESI-MS [CH_3CN] Anal.: 375.1426, Calcd for $C_{24}H_{24}P_2$+H: 375.1426.

2,3,6,7,14,15-Hexamethyl-9-phospha-10-arsatriptycene 6: White solid [m.p. 364~368°C], ^{1}H NMR (600 MHz, $CDCl_3$) δ = 2.19 (18H, s), 7.67 (3H, s), 7.75 (3H, d, $^{3}J_{PH}$ = 10.8 Hz), ^{13}C {^{1}H} NMR (151 MHz, $CDCl_3$) δ = 19.4 (p), 134.7 (t, $^{3}J_{PC}$ = 1.81 Hz), 135.9 (t, $^{2}J_{PC}$ = 46.5 Hz), 136.5 (q, $^{1}J_{PC}$ = 14.3 Hz), 136.6 (q), 140.1 (q, $^{3}J_{PC}$ = 5.1 Hz), 146.4 (q, $^{4}J_{PC}$ = 3.2 Hz), ^{31}P NMR (243 MHz, $CDCl_3$) δ = −34.55 (s), ESI-MS [CH_3CN]: Found: *m/z* 419.0903, Calcd for $C_{24}H_{24}AsP$+H: 419.0904.

2,3,6,7,14,15-Hexamethyl-9-phospha-10-stibatriptycene 7: White solid [m.p. 295~300°C, lit[17] >257~258°C], ^{1}H NMR (600 MHz, $CDCl_3$) δ = 2.18 (s, 9H, CH_3), 2.19 (s, 9H, CH_3), 7.69 (s, 3H), 7.90 (d, $^{3}J_{PH}$ = 12.0 Hz, 3H), ^{31}P{^{1}H} NMR ($CDCl_3$, 243 MHz) δ = −10.8 (s).

2,3,6,7,14,15-Hexamethyl-9-phospha-10-bismatriptycene 8: White solid [m.p. 293~297°C], ^{1}H NMR (600 MHz, $CDCl_3$) δ = 2.17 (9H, s), 2.18 (9H, s), 7.86 (3H, s), 8.29 (3H, d, $^{3}J_{PH}$ = 12.0 Hz), ^{13}C {^{1}H} NMR (151 MHz, $CDCl_3$) δ = 19.2 (p), 19.5 (p), 135.5 (t, $^{1}J_{PC}$ = 53.7 Hz), 136.7(q, $^{2}J_{PC}$ = 16.5 Hz), 137.3 (q, $^{3}J_{PC}$ = 1.51 Hz), 138.4 (t, $^{2}J_{PC}$ = 2.1 Hz), 141.5 (q, $^{3}J_{PC}$ = 5.3 Hz), 163.4 (q), ^{31}P NMR (162 MHz, $CDCl_3$) δ = 12.50 (q, $^{3}J_{PH}$ = 12.2 Hz), ESI-MS [CH_3CN]: Found: *m/z*: 553.1494, Calcd for $C_{24}H_{24}BiP$+H: 553.1492.

4.3 | Synthesis of 9-ethyl-2,3,6,7,14,15-hexamethyl-9-phosphonio-10-heteratriptycene iodide

Under nitrogen, a $CHCl_3$ (5 mL) solution of phosphaheteratriptycenes **1-8** and ethyl iodide (40 μL, 0.500 mmol) was heated at 70°C. $CHCl_3$ (2 mL) was added to the reaction mixture before the reaction solvent was completely evaporated under the reflux condition. The reaction mixture was evaporated after the stirring and the residue was filtrated with THF to give a pale yellow solid of ethylphosphonium iodides **9-16**.

9-Ethyl-2,3,6,7,14,15-hexamethyl-10-phenyl-9-phosphonio-10-silatriptycene iodide 9: White solid [m.p. 307.0-309.0°C], ^{1}H NMR (600 MHz, $CDCl_3$) δ = 2.18 (3H, dt, $^{3}J_{PH}$ = 19.8 Hz, $^{3}J_{HH}$ = 7.2 Hz), 2.25 (9H, s), 2.36 (9H, s), 4.26 (2H, dq, $^{2}J_{PH}$ = 13.8 Hz, $^{3}J_{HH}$ = 7.8 Hz), 7.60 (3H, d, $^{4}J_{HH}$ = 3.6 Hz), 7.80 (2H, tm, $^{3}J_{HH}$ = 7.2 Hz), 7.84 (1H, tm, $^{3}J_{HH}$ = 7.2 Hz), 8.02 (3H, d, $^{3}J_{PH}$ = 12.0 Hz), 8.20 (2H, dm, $^{3}J_{HH}$ = 7.2 Hz), ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ = 7.90 (p, $^{2}J_{PC}$ = 6.20 Hz), 7.95 (s, $^{1}J_{PC}$ = 32.0 Hz), 122.3 (q), 127.2 (q, $^{1}J_{PC}$ = 82.4 Hz), 129.6 (t), 131.5 (t, $^{2}J_{PC}$ = 10.9 Hz), 132.5 (t), 135.3 (t, $^{4}J_{PC}$ = 1.8 Hz), 136.3 (t), 138.8 (q, $^{1}J_{PC}$ = 29.9 Hz), 138.9 (q, $^{3}J_{PC}$ = 7.8 Hz), 140 (q, $^{4}J_{PC}$ = 3.17 Hz), ^{31}P{^{1}H} NMR (243 MHz, $CDCl_3$) δ = −6.15 (s), ^{29}Si{^{1}H} NMR (119 MHz, $CDCl_3$) δ = −40.1 (d, $^{3}J_{PSi}$ = 56.6 Hz), ESI-MS [CH_3CN]: Found: *m/z* 495.2262, Calcd for $C_{32}H_{34}PSi+H_2O$: 495.2268.

9-Ethyl-2,3,6,7,14,15-hexamethyl-10-phenyl-9-phosphonio-10-germatriptycene iodide 10: White solid [m.p. 330.8~331.8°C], ^{1}H NMR (600 MHz, $CDCl_3$) δ = 2.19 (3H, dt, $^{3}J_{PH}$ = 19.2 Hz, $^{3}J_{HH}$ = 7.8 Hz), 2.25 (9H, s), 2.36 (9H, s), 4.27 (2H, dq, $^{2}J_{PH}$ = 13.8 Hz, $^{3}J_{HH}$ = 7.8 Hz), 7.60 (3H, d, $^{4}J_{PH}$ = 3.6 Hz), 7.78-7.80 (3H, m), 8.03 (3H, d, $^{3}J_{PH}$ = 12.0 Hz), 8.06-8.07 (2H, m), ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ = 7.99 (p, $^{2}J_{PC}$ = 5.7 Hz), 8.20 (s, $^{1}J_{PC}$ = 48.2 Hz), 124,4 (q), 124.9 (q), 130.0 (t), 131.8 (t), 132.0 (t, $^{3}J_{PC}$ = 11.0 Hz), 134.5 (t, $^{3}J_{PC}$ = 11.8 Hz), 135.7 (t), 138.8 (q, $^{3}J_{PC}$ = 12.5 Hz), 140.9 (q, $^{3}J_{PC}$ = 3.0 Hz), 142.2 (q, $^{1}J_{PC}$ = 8.5 Hz), ^{31}P{^{1}H} NMR (243 MHz, $CDCl_3$) δ = −9.06 (s), ESI-MS [CH_3CN]: Found: *m/z* 523.1613, Calcd for $C_{32}H_{34}PGe$: 523.1604.

9-Ethyl-2,3,6,7,14,15-hexamethyl-10-phenyl-9-phosphonio-10-stannatriptycene iodide 11: White solid [m.p. 267.5~269.8°C], ^{1}H NMR (600 MHz, $CDCl_3$) δ = 2.16 (3H, dt, $^{3}J_{PH}$ = 18.0 Hz, $^{3}J_{HH}$ = 7.8 Hz), 2.26 (9H, s), 2.37 (9H, s), 4.21 (2H, dq, $^{2}J_{PH}$ = 13.8 Hz, $^{3}J_{HH}$ = 7.2 Hz), 7.65 (3H, d, $^{4}J_{PH}$ = 3.6 Hz, $^{3}J_{SnH}$ = 45.0 Hz), 7.70-7.77 (3H, m), 7.93-7.95 (2H, m), 8.03 (3H, d, $^{3}J_{PH}$ = 12.0 Hz, $^{4}J_{SnH}$ = 20.4 Hz), ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ = 8.6 (p, $^{2}J_{PC}$ = 5.59 Hz), 8.8 (s, $^{1}J_{PC}$ = 49.5 Hz), 19.8 (p), 19.9 (p), 126.0 (q, $^{1}J_{PC}$ = 84.8 Hz), 127.7 (q, $^{4}J_{PH}$ = 4.38 Hz), 130.4 (t, $^{3}J_{SnC}$ = 69.2 Hz), 131.8 (t), 132.7 (t, $^{3}J_{PC}$ = 12.2 Hz, $^{3}J_{SnC}$ = 28.2 Hz), 137.4 (t, $^{3}J_{PC}$ = 12.7 Hz, $^{2}J_{SnC}$ = 27.3 Hz), 137.9 (t, $^{2}J_{SnC}$ = 43.3 Hz), 139.0 (q, $^{3}J_{PC}$ = 13.3 Hz), 141.0 (q, $^{3}J_{PC}$ = 3.17 Hz, $^{3}J_{SnC}$ = 45.3 Hz), 145.0 (q, $^{2}J_{PC}$ = 10.1 Hz), ^{31}P {^{1}H} NMR (243 MHz, $CDCl_3$) δ = −7.79 (t, $^{3}J_{SnP}$ = 302.4 Hz), ^{119}Sn{^{1}H} NMR (224 MHz, $CDCl_3$) δ = −267.7 (d, $^{3}J_{SnP}$ = 302.6 Hz), ESI-MS [CH_3CN]: Found: *m/z* 569.1418, Calcd for $C_{32}H_{34}PSn$: 569.1415.

10-*n*-Butyl-9-ethyl-2,3,6,7,14,15-hexamethyl-9-phosphonio-10-stannatriptycene iodide 12: white solid [decomp. 153~158°C], ^{1}H NMR (600 MHz, $CDCl_3$) δ = 1.15 (3H, t, $^{3}J_{HH}$ = 7.2 Hz), 1,70-1.75 (2H, m), 2.12 (3H, dt, $^{3}J_{PH}$ = 18.6 Hz, $^{3}J_{HH}$ = 7.2 Hz), 2.18-2.21 (2H, m), 2.26 (9H, s), 2.33 (9H, s), 2.43 (2H, t, $^{3}J_{HH}$ = 7.2 Hz), 4.09 (2H, dq, $^{2}J_{PH}$ = 13.2 Hz, $^{3}J_{HH}$ = 7.2 Hz), 7.61 (3H, d, $^{4}J_{PH}$ = 3.6 Hz, $^{3}J_{SnH}$ = 46.2 Hz), 7.93 (3H, d, $^{3}J_{PH}$ = 12.0 Hz, $^{4}J_{SnH}$ = 15.0 Hz), ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ = 8.28 (p, $^{2}J_{PC}$ = 5.89 Hz), 9.05 (s, $^{1}J_{PC}$ = 50.0 Hz), 10.9 (s, $^{4}J_{PC}$ = 3.17 Hz), 13.7 (t), 19.8 (p), 19.9 (p), 27.7 (s), 28.7 (s), 126.0 (q, $^{1}J_{PC}$ = 85.2 Hz), 132.3 (t, $^{3}J_{PC}$ = 12.8 Hz, $^{3}J_{SnC}$ = 26.4 Hz), 137.6 (t, $^{2}J_{SnC}$ = 13.0 Hz), 138.5 (q, $^{3}J_{PC}$ = 13.0 Hz), 140.7 (q, $^{3}J_{PC}$ = 3.17 Hz), 146.1 (q, $^{2}J_{PC}$ = 10.3 Hz), ^{31}P {^{1}H} NMR (243 MHz, $CDCl_3$) δ = −7.37 (t, $^{3}J_{SnP}$ = 237.9 Hz), ^{119}Sn{^{1}H} NMR (224 MHz, $CDCl_3$) δ = −232.3 (d, $^{3}J_{SnP}$ = 257.4 Hz), ESI-MS [CH_3CN]: Found: *m/z* 549.1734, Calcd for $C_{30}H_{38}PSn$: 549.1728.

9-Ethyl-2,3,6,7,14,15-hexamethyl-9-phosphonio-10-phosphphatriptycene iodide 13: Pale yellow solid [m.p.342.5~343.5°C], ^{1}H NMR (600 MHz, $CDCl_3$) δ = 2.15 (3H, dt, $^{3}J_{PH}$= 19.8 Hz, $^{3}J_{HH}$= 7.2 Hz), 2.28 (9H, s), 2.35 (9H, s), 4.29 (2H, dq, $^{2}J_{PH}$= 9.00 Hz, $^{3}J_{HH}$= 7.8 Hz), 7.80 (3H, dd, $^{3}J_{PH}$= 6.6 Hz, $^{4}J_{HH}$= 4.2 Hz), 8.04 (3H, d, $^{3}J_{PH}$= 11.4 Hz), ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ = 7.49 (p, $^{2}J_{PC}$ = 7.35 Hz), 7.90 (s, $^{1}J_{PC}$ = 46.3 Hz), 19.7 (p), 19.8 (p), 124.8 (q, $^{1}J_{PC}$ = 74.7 Hz), 132.1 (t, $^{2}J_{PC}$ = 11.1 Hz), 136.8 (t, $^{2}J_{PC}$ = 33.7 Hz, $^{3}J_{PC}$ = 8.55 Hz), 139.4 (q, $^{3}J_{PC}$ = 12.3 Hz), 140.7 (q, $^{1}J_{PC}$ = 21.1 Hz, $^{2}J_{PC}$ = 10.2 Hz), 141.6 (q, $^{3}J_{PC}$ = 13.4 Hz), ^{31}P {^{1}H}NMR (243 MHz, $CDCl_3$) δ = −2.56 (s), −59.8 (s), ESI-MS [CH_3CN]: Found: *m/z* 403.1742, Calcd for $C_{26}H_{29}P_2$: 403.1739.

9-Ethyl-2,3,6,7,14,15-hexamethyl-9-phosphonio-10-arsatriptycene iodide 14: Pale yellow solid [m.p. 331~334°C], ^{1}H NMR (600 MHz, $CDCl_3$) δ = 2.17 (3H, dt, $^{3}J_{PH}$= 19.2 Hz, $^{3}J_{HH}$= 7.8 Hz), 2.28 (9H, s), 2.36 (9H, s), 4.27 (2H, dq, $^{2}J_{PH}$= 13.8 Hz, $^{3}J_{HH}$= 7.2 Hz), 7.79 (3H, d, $^{4}J_{PH}$= 4.2 Hz), 8.05 (3H, d, $^{3}J_{PH}$= 10.8 Hz), ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ = 7.62 (p, $^{2}J_{PC}$ = 5.74 Hz), 8.34 (s, $^{1}J_{PC}$ = 47.4 Hz), 19.8 (p), 19.9 (p), 122.1 (q, $^{1}J_{PC}$ = 91.7 Hz), 132.2 (t, $^{2}J_{PC}$ = 12.8 Hz), 135.9 (t, $^{3}J_{PC}$ = 9.21 Hz), 139.3 (q, $^{3}J_{PC}$ = 12.1 Hz), 141.5 (q, $^{4}J_{PC}$ = 2.57 Hz), 143.8 (q, $^{2}J_{PC}$ = 6.95 Hz), ^{31}P {^{1}H}NMR (243 MHz, $CDCl_3$) δ = 1.32 (s), ESI-MS [CH_3CN]: Found: *m/z* 447.1214, Calcd for $C_{26}H_{29}AsP$: 447.1217.

9-Ethyl-2,3,6,7,14,15-hexamethyl-9-phosphonio-10-stibatriptycene iodide 15: Pale yellow solid [m.p. 238~341°C, lit[17] m.p. 237~241°C], ^{1}H NMR (600 MHz, $CDCl_3$) δ = 2.16 (dt, $^{3}J_{PH}$ = 18.6 Hz, $^{3}J_{HH}$ = 7.2 Hz, 3H, H_{Et}), 2.27 (s, 9H, H_{Me}), 2.36 (s, 9H, H_{Me}), 2.36 (s, 9H, H_{Me}), 4.20 (dq, $^{2}J_{PH}$ = 13.2 Hz, $^{3}J_{HH}$ = 7.6 Hz, 2H, H_{Et}), 7.85 (d, $^{4}J_{PH}$ = 3.6 Hz, 3H, 4,5,16-H), 8.01 (d, $^{3}J_{PH}$ = 10.8 Hz, 3H, 1,8,13-H), ^{31}P{^{1}H} NMR (243 MHz, $CDCl_3$) δ = 12.2 (s).

9-Ethyl-2,3,6,7,14,15-hexamethyl-9-phosphonio-10-bismatriptycene iodide 16: pale yellow solid [m.p. 293~295°C (decomp.)], ^{1}H NMR (600 MHz, $CDCl_3$) δ = 2.13 (3H, dt, $^{3}J_{PH}$ = 17.6 Hz, $^{3}J_{HH}$ = 7.52 Hz), 2.27 (9H, s), 2.29 (9H, s), 3.81 (2H, dq, $^{2}J_{PH}$ = 13.5 Hz, $^{3}J_{HH}$ = 7.59 Hz), 8.11 (3H, d, $^{3}J_{PH}$ = 10.2 Hz), 8.29 (3H, d, $^{4}J_{PH}$ = 3.0 Hz), ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ = 7.67 (p, $^{3}J_{PC}$ = 5.74 Hz), 10.6 (s, $^{2}J_{PC}$ = 49.7 Hz), 19.73 (p), 19.92 (p), 122.8 (t, $^{1}J_{PC}$ = 94.6 Hz), 131.6(q, $^{2}J_{PC}$ = 14.3 Hz), 138.2 (q, $^{3}J_{PC}$ = 12.2 Hz), 139.2 (t, $^{3}J_{PC}$ = 12.2 Hz), 142.3 (q, $^{4}J_{PC}$ = 3.62 Hz), 159.0 (q), ^{31}P NMR (162 MHz, $CDCl_3$) δ = 54.4 (s), ESI-MS [CH_3CN]: Found: *m/z* 581.1807, Calcd for $C_{26}H_{29}Bi$: 581.1805.

4.4 | Data of 2,3,6,7,14,15-Hexamethyl-9-phospha-10-heteratriptycene 9-oxide

Phosphaheteratriptycene oxides were purified from the crude materials, which were obtained by Wittig reactions of non-stabilized phosphonium ylides bearing a phosphaheteratriptycene skeleton with benzaldehyde, by the following method. The crude materials were obtained by evaporation of THF as a reaction solvent and filtrated with a membrane together with 3 mL of $CHCl_3$. The $CHCl_3$ solution was introduced to a 908 gel permeation chromatography (GPC) and separated a few fraction to get a fraction containing a target phosphine oxide with a retention time at 45-50 min. The obtained fraction was separated by preparative thin layer chromatography (PTLC) to get a pure target phosphine oxide.

2,3,6,7,14,15-Hexamethyl-10-phenyl-9-phospha-10-silatriptycene 9-oxide 33: compound **33** decomposed during its purification because of unstable in the air.

2,3,6,7,14,15-Hexamethyl-10-phenyl-9-phospha-10-germatriptycene 9-oxide 34: Pale yellow solid [decomp. 313.0~314.5°C], ^{1}H NMR (600 MHz, $CDCl_3$) δ = 2.20 (9H, s), 2.25 (9H, s), 7.48 (3H, d, $^{4}J_{PH}$ = 3.6 Hz), 7.69-7.74 (3H, m), 8.04 (3H, d, $^{2}J_{PH}$ = 12.0 Hz), 8.07-8.09 (2H, m), ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ = 19.5 (p), 19.7 (p), 127.4 (q, $^{4}J_{PC}$ = 3.17 Hz), 129.4 (t), 130.8 (t), 131.0 (t, $^{2}J_{PC}$ = 7.7 Hz), 133.0 (t, $^{3}J_{PC}$ = 12 Hz), 134.5 (q), 135.94 (t), 135.97 (q, $^{1}J_{PC}$ = 100.1 Hz), 136.8 (q, $^{3}J_{PC}$ = 11.5 Hz), 137.7 (q, $^{4}J_{PC}$ = 2.3 Hz), 142.2 (q, $^{2}J_{PC}$ =12.4 Hz), ^{31}P{^{1}H} NMR (243 MHz, $CDCl_3$) δ = 1.65 (s), ESI-MS [CH_3CN]: Found: *m/z* 511.1241, Calcd for $C_{30}H_{29}GeOP$+H: 511.1241.

2,3,6,7,14,15-Hexamethyl-10-phenyl-9-phospha-10-stannatriptycene 9-oxide 35: White solid [m.p 305.1~307.9°C], ^{1}H NMR (600 MHz, $CDCl_3$) δ = 2.21 (9H, s), 2.26 (9H, s), 7.54 (3H, d, $^{4}J_{PH}$ = 3.60 Hz), 7.64-7.69 (3H, m), 7.94-7.75 (2H, m), 8.14 (3H, d, $^{3}J_{PH}$ = 11.4 Hz, $^{4}J_{SnH}$ = 19.8 Hz), ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ = 19.48 (p), 19.54 (p), 129.8 (t), 130.8 (t), 131.9 (t, $^{2}J_{PC}$ = 8.15 Hz), 136.00 (t, $^{3}J_{PC}$ = 13.4 Hz),

136.01 (q), 137.0 (q), 137.3 (q, $^{1}J_{PC}$ = 90.1 Hz), 137.9 (q, $^{4}J_{PC}$ = 3.02 Hz), 138.2 (t), 144.2 (q), $^{31}P\{^{1}H\}$ NMR (242 MHz, $CDCl_3$) δ = 1.99 (t, $^{3}J_{PSn}$ = 305.1 Hz), $^{119}Sn\{^{1}H\}$ NMR (223 MHz, $CDCl_3$) δ = -282.9 (d, $^{3}J_{PSn}$ = 315.1 Hz), ESI-MS [CH_3CN]: Found: *m/z* 557.1056, Calcd for $C_{30}H_{29}OPSn$: 557.1051.

10-*n*-Butyl-2,3,6,7,14,15-hexamethyl-9-phospha-10-stannatriptycene 9-oxide 36: White solid [m.p. 289~292°C (decomp.)], ^{1}H NMR (600 MHz, $CDCl_3$) δ = 1.12 (3H, t, $^{2}J_{HH}$ = 7.2 Hz), 1.69-1.74 (2H, m), 2.10-2.25 (2H, m), 2.21 (9H, s), 2.23 (9H, s), 2.29-2.30 (2H, m), 7.45 (3H, dt, $^{4}J_{PH}$ = 3.60 Hz, $^{4}J_{SnH}$ = 14.0 Hz), 8.09 (3H, dt, $^{3}J_{PH}$ = 11.4 Hz, $^{4}J_{SnH}$ = 11.4 Hz), $^{31}P\{^{1}H\}$ NMR (242 MHz, $CDCl_3$) δ = 3.61 (t, $^{3}J_{PSn}$ = 267.0 Hz), $^{119}Sn\{^{1}H\}$ NMR (223 MHz, $CDCl_3$) δ = −249.4 (d, $^{3}J_{PSn}$ = 266.0 Hz), ESI-MS [CH_3CN]: Found: *m/z* 537.1367, Calcd for $C_{28}H_{33}OPSn$+H: 537.1364.

2,3,6,7,14,15-Hexamethyl-9,10-diphosphatriptycene 9-oxide 37: Pale yellow solid [decomp. 325~330°C], ^{1}H NMR (600 MHz, $CDCl_3$) δ = 2.26 (9H, s), 2.25 (9H, s), 7.62 (3H, dd, $^{3}J_{PH}$ = 10.8 Hz, $^{4}J_{PH}$ = 4.8 Hz), 7.90 (3H, d, $^{3}J_{PH}$ = 11.4 Hz), $^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$) δ = 19.5 (p), 19.6 (p), 130.9 (t, $^{2}J_{PC}$ = 8.0 Hz), 134.7 (q, $^{1}J_{PC}$ = 105.5 Hz), 135.5 (t, $^{1}J_{PC}$ = 41.4 Hz, $^{2}J_{PC}$ = 9.21 Hz), 137.5 (q, $^{3}J_{PC}$ = 10.7 Hz), 138.2 (q, $^{3}J_{PC}$ = 13.4 Hz, $^{4}J_{PC}$ = 2.27 Hz), 140.9 (q, $^{2}J_{PC}$ = 11.8 Hz, $^{3}J_{PC}$ = 9.60 Hz), ^{31}P NMR (243 MHz, $CDCl_3$) δ = −74.1 (d, $^{3}J_{PP}$ = 4.8 Hz), 7.97 (d, $^{3}J_{PP}$ = 5.1 Hz), ESI-MS [CH_3CN] : Found: *m/z* 391.1383, Calcd for $C_{24}H_{24}OP_2$+H: 391.1375.

2,3,6,7,14,15-Hexamethyl-9-phospha-10-arsatriptycene 9-oxide 38: White solid [decomp. 275-280°C], ^{1}H NMR (600 MHz, $CDCl_3$) δ = 2.23 (9H, s), 2.25 (9H, s), 7.60 (3H, d, $^{4}J_{PH}$ = 4.8 Hz), 7.95 (3H, d, $^{3}J_{PH}$ = 10.8 Hz), $^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$) δ = 19.4 (p), 19.6 (p), 131.2 (t, $^{2}J_{PC}$ = 8.6 Hz), 132.0 (q, $^{1}J_{PC}$ = 107.8 Hz), 134.7 (q, $^{3}J_{PC}$ = 10.1 Hz), 137.4 (q, $^{3}J_{PC}$ = 11.3 Hz), 138.2 (q, $^{4}J_{PC}$ = 2.27 Hz), 143.2 (q, $^{2}J_{PC}$ = 13.1 Hz), ^{31}P NMR (243 MHz, $CDCl_3$) δ = 12.1 (s), ESI-MS [CH_3CN]: Found: *m/z* 435.0854, Calcd for $C_{24}H_{24}AsOP$+H: 435.0853.

2,3,6,7,14,15-Hexamethyl-9-phospha-10-stibatriptycene 9-oxide 39: Pale yellow solid [decomp. 281~284°C, lit[17] decomp. 284~285°C], ^{1}H NMR ($CDCl_3$, 600 MHz) δ = 2.22 (s, 9H, CH_3), 2.25 (s, 9H, CH_3), 7.66 (d, $^{4}J_{PH}$ = 4.2 Hz, 3H, 4,5,16-H), 8.09 (d, $^{3}J_{PH}$ = 10.8 Hz, 3H, 1,8,13-H), $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 243 MHz) δ = 22.7 (s).

2,3,6,7,14,15-Hexamethyl-9-phospha-10-bismatriptycene 9-oxide 40: White solid [m.p. >300°C], ^{1}H NMR (400 MHz, $CDCl_3$) δ = 2.25 (9H, s), 2.27 (9H, s), 8.0 (3H, d, $^{4}J_{PH}$ = 4.0 Hz), 8.40 (3H, d, $^{3}J_{PH}$ = 8.0 Hz), ^{31}P NMR (162 MHz, $CDCl_3$) δ = 65.3 (s), ESI-MS [CH_3CN]: Found: *m/z* 569.1446, Calcd for $C_{24}H_{24}BiOP$+H: 569.1441.

4.5 | The Wittig reactions of non-stabilized phosphonium ylides with PhCHO at −90°C and VT-$^{31}P\{^{1}H\}$ NMR spectroscopy

Ethylphosphonium salts **9-16** in THF (0.5 mL) as a reaction solvent were placed in a J-Young NMR tube with a sealed capillary tube filled with acetone-d_6 as a lock solvent for ^{1}H and ^{31}P NMR measurement. To a suspension of **9-16** in THF in the NMR tube was added $(TMS)_2NNa$ at 0°C to generate non-stabilized phosphonium ylides **17-24** making the solution yellow. The phosphonium ylides **17-24** were reacted with PhCHO at −90°C. VT-$^{31}P\{^{1}H\}$ NMR spectra of the reaction mixture were measured every 10°C from −90°C to 25°C by accumulation on 128 of scan number after the addition of PhCHO to THF solution at −90°C. The measurements at each target temperature were performed after ca. 5 min for getting the constant temperature by the thermo-monitor in an NMR equipment. The mixture was allowed to warm to room temperature for over 3 hours. Yields were estimated by using a singlet signal due to the methylene protons of $Ph_2C{=}CH_2$ in THF (0.1 mL) as an internal standard in ^{1}H NMR spectroscopy after the confirmation of no change of the spectra in the Wittig reaction for over 12 hours.

(1) 17 + PhCHO: ethylphosphonium iodide **9** bearing the *Si*-phenylphosphasilatriptycene (10.4 mg, 17.2 μmol), $(TMS)_2NNa$ (36 μL, 68 μmol), PhCHO (5.9 μL, 6.1 mg, 57.6 μmol), $PhCH{=}CHCH_3$ (0.772 mg, 6.54 μmol)/$Ph_2C{=}CH_2$ (2.21 mg, 12.3 μmol) = 0.531/1.00, Yield 38%, (*Z*):(*E*) = 62:38.

(2) 18 + PhCHO: ethylphosphonium iodide **10** bearing the *Ge*-phenylphosphagermatriptycene (12.6 mg, 21.0 μmol), $(TMS)_2NNa$ (36 μL, 68 μmol), PhCHO (5.9 μL, 6.1 mg, 57.6 μmol), $PhCH{=}CHCH_3$ (1.78 mg, 15.1 μmol)/$Ph_2C{=}CH_2$(2.04 mg,11.3 μmol) = 1.34/1.00, Yield 72%, (*Z*):(*E*) = 17:83.

(3) 19 + PhCHO: ethylphosphonium iodide **11** bearing the *Sn*-phenylphosphastannatriptycene (10.9 mg, 15.0 μmol), $(TMS)_2NNa$ (36 μL, 68 μmol), PhCHO (5.9 μL, 6.1 mg, 57.6 μmol), $PhCH{=}CHCH_3$ (0.602 mg, 5.1 μmol)/$Ph_2C{=}CH_2$ (2.11 mg, 11.7 μmol) = 0.436/1.00, Yield 34%, (*Z*):(*E*) = 21:79.

(4) 20 + PhCHO: ethylphosphonium iodide **12** bearing the *Sn*-*n*-butylphosphastannatriptycene (11.9 mg, 17.7 μmol), $(TMS)_2NNa$ (36 μL, 68 μmol), PhCHO (5.9 μL, 6.1 mg, 57.6 μmol), $PhCH{=}CHCH_3$ (0.940 mg, 7.97 μmol)/$Ph_2C{=}CH_2$ (2.23 mg, 12.3 μmol) = 0.633/1.00, Yield 45%, (*Z*):(*E*) = 26:74.

(5) 21 + PhCHO: ethylphosphonium iodide **13** bearing the diphosphatriptycene (10.2 mg, 19.2 μmol), $(TMS)_2NNa$ (36 μL, 68 μmol), PhCHO (5.9 μL, 6.1 mg, 57.6 μmol), $PhCH{=}CHCH_3$ (0.340 mg, 2.88 μmol)/$Ph_2C{=}CH_2$ (2.05 mg, 11.4 μmol) = 0.252/1.00, Yield 15%, (*Z*):(*E*) = 51:49.

TABLE 3 Crystal data of phenylphosphastannatriptycenes **3** and **11**

	3	**11**
M.F.	$C_{30}H_{29}SnP$	$C_{32}H_{34}ISnP{\cdot}2.5C_6H_6$(benzene)
Formula weight	539.19	890.42
Temperature	120	120
Wavelength	0.71073	0.71073
Crystal system	*Monoclinic*	*Triclinic*
Space group	*P*21/c	*P*-1
a (Å)	9.8994(4)	12.7444(14)
b (Å)	11.646(5)	13.4628(15)
c (Å)	21.7943(10)	13.4777(15)
α (°)	90	102.3488(15)
β (°)	94.9660(5)	111.7726(13)
γ (°)	90	99.5412(15)
Volume (Å^3)	2503.33(19)	2019.8(4)
Z	4	2
Density (g/cm^3)	1.431	1.464
Crystal size	0.50 × 0.43 × 0.33	0.52 × 0.51 × 0.03
Index ranges	−13 < =h<=9, −13 < =k<=15, −20 < =l<=29	−16 < =h<=14, −14 < =k<=18, −18 < =l<=17
Reflections collected	14364	11561
Data/parameters	5882/295	9014/458
GOF	1.041	1.036
R (all data)	0.0219	0.0377
*wR*2 (all data)	0.0494	0.0686

(6) **22** + PhCHO: ethylphosphonium iodide **14** bearing the phosphaarsatriptycene (11.4 mg, 19.9 μmol), $(TMS)_2NNa$ (36 μL, 68 μmol), PhCHO (5.9 μL, 6.1 mg, 57.6 μmol), $PhCH{=}CHCH_3$ (0.742 mg, 6.29 μmol)/$Ph_2C{=}CH_2$ (2.38 mg, 13.2 μmol) = 0.477/1.00, Yield 32%, (*Z*):(*E*) = 35:65.

(7) **23** + PhCHO: ethylphosphonium iodide **15** bearing the phosphastibatriptycene (11.8 mg, 19.0 μmol), $(TMS)_2NNa$ (36 μL, 68 μmol), PhCHO (5.9 μL, 6.1 mg, 57.6 μmol), $PhCH{=}CHCH_3$ (1.95 mg, 16.5 μmol)/$Ph_2C{=}CH_2$ (1.70 mg, 9.44 μmol) = 1.75/1.00, Yield 87%, (*Z*):(*E*) = 13:87.[17–19]

(8) **24** + PhCHO: ethylphosphonium iodide **16** bearing the phosphabismatriptycene (10.0 mg, 14.1 μmol), $(TMS)_2NNa$ (30 μL, 57 μmol), PhCHO (5.9 μL, 6.1 mg, 57.6 μmol), $PhCH{=}CHCH_3$ (0.698 mg, 5.92 μmol)/$Ph_2C{=}CH_2$ (2.20 mg, 12.2 μmol) = 0.485/1.00, Yield 42%, (*Z*):(*E*) = 26:74.

4.6 | The Wittig reactions of non-stabilized phosphonium ylides with PhCHO at 0°C

Ethylphosphonium salts **9-16** in THF (0.5 mL) in the NMR tube were added $(TMS)_2NNa$ at 0°C to generate non-stabilized phosphonium ylides **17-24**, which were reacted with PhCHO at 0°C. Yields were estimated by the same way in the reaction at −90°C.

(1) **17** + PhCHO: ethylphosphonium iodide **9** bearing the *Si*-phenylphosphasilatriptycene (3.94 mg, 8.25 μmol), $(TMS)_2NNa$ (22 μL, 41 μmol), PhCHO (3.9 μL, 4.1 mg, 38.4 μmol), $PhCH{=}CHCH_3$ (0.459 mg, 3.89 μmol)/$Ph_2C{=}CH_2$ (2.24 mg, 12.4 μmol) = 0. 314/1.00, Yield 47%, (*Z*):(*E*) = 87:13.

(2) **18** + PhCHO: ethylphosphonium iodide **10** bearing the *Ge*-phenylphosphagermatriptycene (3.53 mg, 6.76 μmol), $(TMS)_2NNa$ (22 μL, 41 μmol), PhCHO (3.9 μL, 4.1 mg, 38.4 μmol), $PhCH{=}CHCH_3$ (0.435 mg, 3.69 μmol)/$Ph_2C{=}CH_2$ (2.05 mg, 14.9 μmol) = 0.324/1.00, Yield 55%, (*Z*):(*E*) = 22:78.

(3) **19** + PhCHO: ethylphosphonium iodide **11** bearing the *Sn*-phenylphosphastannatriptycene (10.2 mg, 17.5 μmol), $(TMS)_2NNa$ (36 μL, 68 μmol), PhCHO (5.9 μL, 6.1 mg, 57.6 μmol), $PhCH{=}CHCH_3$ (1.16 mg, 9.87 μmol)/$Ph_2C{=}CH_2$ (2.09 mg, 11.6 μmol) = 0.850/1.00, Yield 55%, (*Z*):(*E*) = 12:88.

(4) **20** + PhCHO: ethylphosphonium iodide **12** bearing the *Sn-n*-butylphosphastannatriptycene (10.5 mg, 15.6 μmol), $(TMS)_2NNa$ (36 μL, 68 μmol), PhCHO

TABLE 4 Free energies and phosphorus-31 NMR chemical shifts of 1,2-oxaphosphetanes

M	Si (*cis*-form)	Si (*trans*-form)	P (*cis*-form)	P (*trans*-form)
$G_{at\ 298\ K}$ (hartree)[a]	−1979.378874	−1979.382149	−1799.652164	−1799.655453
ΔG^0 (kcal/mol)	0	−2.06	0	−2.06
Imaginary Freq.[a]	0	0	0	0
M–P (Å)	3.160	3.164	3.263	3.269
^{31}P NMR (ppm)[b]	437.550	434.458	437.812	435.305
δ_P (from H_3PO_4[c])	−67.7	−64.6	−59.5	−56.9
δ_P (observation)	−81.8	−80.0	−80.1	−78.2
M	**Ge (*cis*-form)**	**Ge (*trans*-form)**	**As (*cis*-form)**	**As (*trans*-form)**
$G_{at\ 298\ K}$ (hartree)[a]	−1693.597771	−1693.601332	−1464.383150	−1464.386524
ΔG^0 (kcal/mol)	0	−2.23	0	−2.12
Imaginary Freq.[a]	0	0	0	0
M–P (Å)	3.204	3.208	3.364	3.370
^{31}P NMR (ppm)[b]	441.709	438.639	435.245	432.317
δ_P (from H_3PO_4[c])	−71.8	−68.8	−56.9	−54.0
δ_P (observation)	−82.8	−81.0	−73.4	−71.3
M	**Sn (*cis*-form)**	**Sn (*trans*-form)**	**Sb (*cis*-form)**	**Sb (*trans*-form)**
$G_{at\ 298\ K}$ (hartree)[a]	−1693.178790	−1693.182383	−1463.653813	−1463.657380
ΔG^0 (kcal/mol)	0	−2.25	0	−2.24
Imaginary Freq.[a]	0	0	0	0
M–P (Å)	3.317	3.321	3.473	3.437
^{31}P NMR (ppm)[b]	436.566	434.574	424.093	421.413
δ_P (from H_3PO_4[c])	−66.7	−64.7	−45.7	−43.1
δ_P (observation)	−76.2	−74.8	−57.3	−55.2
M	**Pb (*cis*-form)**	**Pb (*trans*-form)**	**Bi (*cis*-form)**	**Bi (*trans*-form)**
$G_{at\ 298\ K}$ (hartree)[a]	−1693.231692	−1693.235336	−1463.691071	−1463.694594
ΔG^0 (kcal/mol)	0	−2.29	0	−2.21
Imaginary Freq.[a]	0	0	0	0
M–P (Å)	3.358	3.363	3.559	3.564
^{31}P NMR (ppm)[b]	437.253	435.198	397.738	395.074
δ_P (from H_3PO_4[c])	−67.4	−65.3	−19.4	−16.7
δ_P (observation)	No data	No data	−14.2	−12.8

[a]Optimization and frequency analysis by B3LYP/6-31G(d) for C, H, Si, P, and O, lanl2dz for Ge, Sn, Pb, As, Sb, and Bi.
[b]GIAO method for NMR by B3LYP/6-31G(d) for C, H, O, and P(1,2-oxaphosphetane), DZP for Si, Ge, Sn, Pb, P(bridgehead atom), As, Sb, and Bi.
[c]The phosphorus-31 chemical shift standard; δ_P 369.885 for H_3PO_4.

(5.9 μL, 6.1 mg, 57.6 μmol), PhCH=CHCH$_3$ (0.864 mg, 7.32 μmol)/Ph$_2$C=CH$_2$ (2.37 mg, 13.2 μmol) = 0.550/1.00, Yield 47%, (*Z*):(*E*) = 11:89.

(5) **21** + PhCHO: ethylphosphonium iodide **13** bearing the diphosphatriptycene (2.36 mg, 5.85 μmol), (TMS)$_2$NNa (22 μL, 41 μmol), PhCHO (3.9 μL, 4.1 mg, 38.4 μmol), PhCH=CHCH$_3$ (0.396 mg, 3.36 μmol)/Ph$_2$C=CH$_2$ (2.24 mg, 12.4 μmol) = 0.270/1.00, Yield 57%, (*Z*):(*E*) = 48:52.

(6) **22** + PhCHO: ethylphosphonium iodide **14** bearing the phosphaarsatriptycene (3.61 mg, 8.07 μmol), (TMS)$_2$NNa (22 μL, 41 μmol), PhCHO (3.9 μL, 4.1 mg, 38.4 μmol), PhCH=CHCH$_3$ (0.480 mg, 4.07 μmol)/Ph$_2$C=CH$_2$ (2.05 mg, 14.9 μmol) = 0.272/1.00, Yield 50%, (*Z*):(*E*) = 36:64.

(7) **23** + PhCHO: ethylphosphonium iodide **15** bearing the phosphastibatriptycene (10.9 mg, 17.6 μmol), (TMS)$_2$NNa (36 μL, 68 μmol), PhCHO (5.9 μL, 6.1 mg, 57.6 μmol), PhCH=CHCH$_3$ (1.45 mg, 12.3 μmol)/Ph$_2$C=CH$_2$ (2.37 mg, 13.2 μmol) = 0.932/1.00, Yield 70%, (*Z*):(*E*) = 20:80.

(8) **24** + PhCHO: ethylphosphonium iodide **16** bearing the phosphabismatriptycene (10.2 mg, 17.5 μmol), (TMS)$_2$NNa (36 μL, 68 μmol), PhCHO (5.9 μL, 6.1 mg,

57.6 μmol), $PhCH{=}CHCH_3$ (1.20 mg, 10.2 μmol)/ $Ph_2C{=}CH_2$ (2.09 mg, 11.6 μmol) = 0.877/1.00, Yield 58%, (*Z*):(*E*) = 25:75.

4.7 | X-ray crystallographic analysis

Single crystals of **3** and **11** were grown by the slow evaporation at room temperature, respectively. A colorless block crystal for each of **3** and **11** having approximate dimensions of $0.50 \times 0.43 \times 0.33$ and $0.53 \times 0.52 \times 0.23$ mm^3, respectively, was mounted on a glass fiber. All measurements were carried out on a Bruker AXS Inc. SMART APEX II with graphite monochromated Mo-Kα radiation (λ = 0.71073 Å). The structure was solved by direct methods and expanded using Fourier techniques. All non-hydrogen atoms were refined anisotropically, while hydrogen atoms were refined isotropically. Crystallographic data are summarized in Table 3.

Crystallographic data for **3** and **11** have been deposited with Cambridge Crystallographic Data Centre: CCDC 1870406 and 1870407 for **3** and **11**. These data can be obtained free of charge *via* http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; Fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk).

ACKNOWLEDGMENTS

This study was partially supported by a Grant-in-Aid for Encouragement of Young Scientists (B) to Y. U. (No. 16750041 and No. 18750037) from the Ministry of Education, Culture, Sports, Science, and Technology of Japan, the Ogasawara Foundation for Oversea Visiting Researchers, the Mikiya Foundation for Oversea Visiting Researchers, the Murata Science Foundation, and Kitasato University Research Grant for Young Researchers. The author, Y. U., thanks Emeritus Professor Takayuki Kawashima for useful advice. The authors would like to thank Editage (www.editage.jp) for English language editing.

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How to cite this article: Uchiyama Y, Kuniya S, Watanabe R, Ohtsuki T. Heteroatom effects toward isomerization of intermediates in wittig reactions of non-stabilized phosphonium ylides bearing a phosphaheteratriptycene skeleton with benzaldehyde. *Heteroatom Chem*. 2018;e21473. https://doi.org/10.1002/hc.21473