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(*E*)-Selective Wittig Reactions of a Non-stabilized Phosphonium Ylide Bearing a Phosphastibatriptycene Skeleton with Benzaldehydes

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Dedicated to Professor Takayuki Kawashima on the occasion of his 70th birthday

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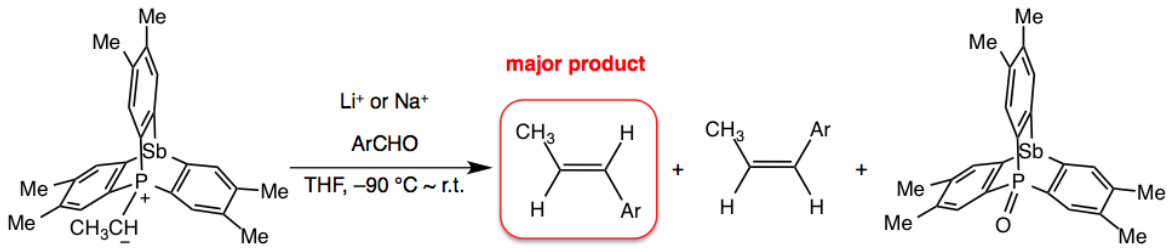
The Wittig reactions of a non-stabilized phosphonium ylide bearing a phosphastibatriptycene skeleton with benzaldehydes provided selectively (*E*)-alkenes in the presence of Li and Na salts. **VT-^{31}P{^{1}H} NMR spectra** in the presence of Li and Na salts showed two signals assigned to the *cis*- and *trans*-1,2-oxaphosphetanes, respectively, and the existence of equilibrium these intermediates at –40 °C.



Abstract

The Wittig reactions of a non-stabilized phosphonium ylide bearing a phosphastibatriptycene skeleton, regarded as a tridentate aryl ligand, with benzaldehydes gave (*E*)-alkenes with high selectivity in the presence of both lithium and sodium salts. As previously reported, the reactions of a triphenylphosphonium ylide with benzaldehydes under the same conditions afforded mainly (*Z*)-alkenes. Variable temperature (VT)-^{31}P{^{1}H} NMR spectra showed two signals, assigned to *cis*- and *trans*-1,2-oxaphosphetanes, which were observed at different temperatures, –80 °C and –40 °C, respectively, in the Wittig reaction of the non-stabilized phosphonium ylide bearing a phosphastibatriptycene skeleton with benzaldehyde, in the

presence of both lithium and sodium salts, and showed the existence of equilibrium between these products at –40 °C. On the other hand, this equilibrium was not clearly observed in the reaction of the triphenylphosphonium ylide with benzaldehyde, for which only one signal was detected. The observed intermediates were confirmed to be 1,2-oxaphosphetanes by deprotonations of the isolated *β*-hydroxyalkylphosphonium salts bearing a phosphastibatriptycene skeleton and triphenylphosphine moiety, respectively. Crossover reactions were conducted in the deprotonations of *β*-hydroxyalkylphosphonium salts using TMS_2NNa in the presence of *p*-chlorobenzaldehyde, to observe the signals of 1,2-oxaphosphetanes containing phenyl and *p*-chlorophenyl groups at the 4-positions, indicating the exchange process between benzaldehyde and *p*-chlorobenzaldehyde at –40 °C for the phosphastibatriptycene system and at 0 °C for triphenyl derivatives. These results clearly indicated that stereochemical drift occurred at those temperatures, even in reactions using non-stabilized phosphonium ylides. The stereochemical drift in the phosphastibatriptycene system occurred at a lower temperature than for the triphenyl derivative, explaining the (*E*)-selective Wittig reaction of the non-stabilized phosphonium ylide bearing a phosphastibatriptycene skeleton with benzaldehydes in the presence of lithium and sodium salts.

Keywords

Wittig reaction, Non-stabilized phosphonium ylide, Tridentate aryl ligand, VT-$^{31}P\{^1H\}$ NMR spectroscopy, 1,2-Oxaphosphetane, Stereochemical drift

Introduction

The Wittig reaction has been used to prepare alkenes in the fields of organic synthesis and natural product synthesis, and catalytic reactions have also been developed.[1-3] Mechanistic studies have also been carried out as an academically attractive issue to enable to control the selectivity of (*E*)- and (*Z*)-alkene formation.[4] Since the stereoselectivity of the product of the Wittig reaction depends on the kinds of used ylides, the selection of phosphonium ylides is important to obtain target alkenes with the desired stereochemistry around the carbon–carbon double bond.[4] Although the previous investigations on 1,2-oxaphosphetanes have revealed the substituent effects on phosphorus and carbons at the 3- and 4-positions of the 1,2-oxaphosphetane ring, the reaction mechanism has been complicated by the existence of two steps, the formation and decomposition of 1,2-oxaphosphetanes, that are required to obtain alkenes from phosphonium ylides and

carbonyl compounds.[5)]

The mechanistic studies on the Wittig reaction have been carried out energetically since the report on bidentate ligands effective to detect and isolate 1,2-oxaphosphetanes, the sole detected intermediates having a trigonal bipyramidal (TBP) structure.[6)] For example, Vedejs *et al.* developed a dibenzophosphole system containing a bidentate ligand, which was used it to stabilize the intermediates. As a result, they detected the 1,2-oxaphosphetane with a vinyl group at the 3-position, which can be recognized as an intermediate in the reaction of a semi-stabilized phosphonium ylide with an aldehyde, for the first time by ^{31}P NMR spectroscopy, in sharp contrast to semi-stabilized triphenylphosphonium ylides.[7)] 1,2-Oxaphosphetane bearing a methoxycarbonyl group at the 3-position, recognized as the intermediate in the reaction of a stabilized phosphonium ylide with a carbonyl compound was isolated by Kawashima *et al.*[8,9)] The isolated 3-methoxycarbonyl-1,2-oxaphosphetane bearing the Martin ligand decomposed thermally to give the corresponding alkene and phosphine oxide at the rate 52,200 times faster than that of the hydrogen substituted 1,2-oxaphosphetane, which corresponded with the intermediate of the reaction of a non-stabilized phosphonium ylide with a carbonyl compound.[8,9)]

The most important and curious phenomenon in the Wittig reaction is stereochemical drift, which causes the differences between the ratio of the generated initial intermediates, *trans*- and *cis*-1,2-oxaphosphetanes, and that of the resulting (*E*)- and (*Z*)-alkenes, suggesting the existence of an equilibrium between the 1,2-oxaphosphetanes and the starting phosphonium ylide–aldehyde mixture at the first step of the reaction.[4,12)] Stereochemical drift was observed in the Wittig reactions of non-stabilized phosphonium ylides with aromatic aldehydes, in marked contrast to those with aliphatic aldehydes, where the intermediates do not revert to starting materials.[13,14)] In a triphenylphosphine system, the (*Z*)-alkene was obtained as the major product in the presence of lithium and sodium salts.[15)] The ratios of the obtained (*E*)- and (*Z*)-alkenes, 41:59 in the presence of lithium salt and 4:96 in the presence of sodium salt, which were different from those of *trans*- and *cis*-1,2-oxaphosphetanes, 25:75 in the presence of lithium salt and 2:98 in the presence of sodium salt.[15)] On the other hand, a trialkylphosphine system showed more dramatically stereochemical drift than a triphenyl system, namely, the Wittig reaction using a non-stabilized trialkylphosphonium ylide in the presence of lithium and sodium salts favors (*E*)-alkenes, rather than (*Z*)-alkenes, as the major product. In fact, in the reaction under salt-free condition, where the intermediary *trans*- and *cis*-1,2-oxaphosphetanes were observed by Maryanoff *et al*,[16)] the ratio of (*E*)- and (*Z*)-alkenes was 90:10, which was much more

different from that (53:47) of *trans*- and *cis*-1,2-oxaphosphetanes, suggesting that back to the starting phosphonium ylide-aromatic aldehyde mixture occurred more readily in the trialkylphosphine system than in the triphenyl system.[4,15] These results indicated that the degree of stereochemical drift depends on the relative stability among the phosphonium ylide, aldehyde, and intermediary 1,2-oxaphosphetane.

There are two possible mechanisms for the formation of 1,2-oxaphosphetanes at the initial step of the reaction, which makes understanding of the mechanism difficult. One is a [2+2] cycloaddition of a phosphorus ylide with a carbonyl compound and the other is the stepwise cyclization *via* a betaine intermediate.[4,17] While the [2+2] mechanism has been shown to be the best description of the Li-free reactions and the betaine route has been disproven for those cases, this is not the situation for Li-containing cases where the mechanism has not been revealed completely.[18] These results have prompted us to attempt establishing a unifying interpretation on the mechanism of the Wittig reaction.[15–26] We focused on a tridentate ligand around the phosphorus atom like a phosphastibatriptycene skeleton,[10,11] which might affect the stability of the phosphonium ylide and 1,2-oxaphosphetane differently to the previous ligands. Using a system containing such a ligand will provide important information on the mechanism of the Wittig reaction.

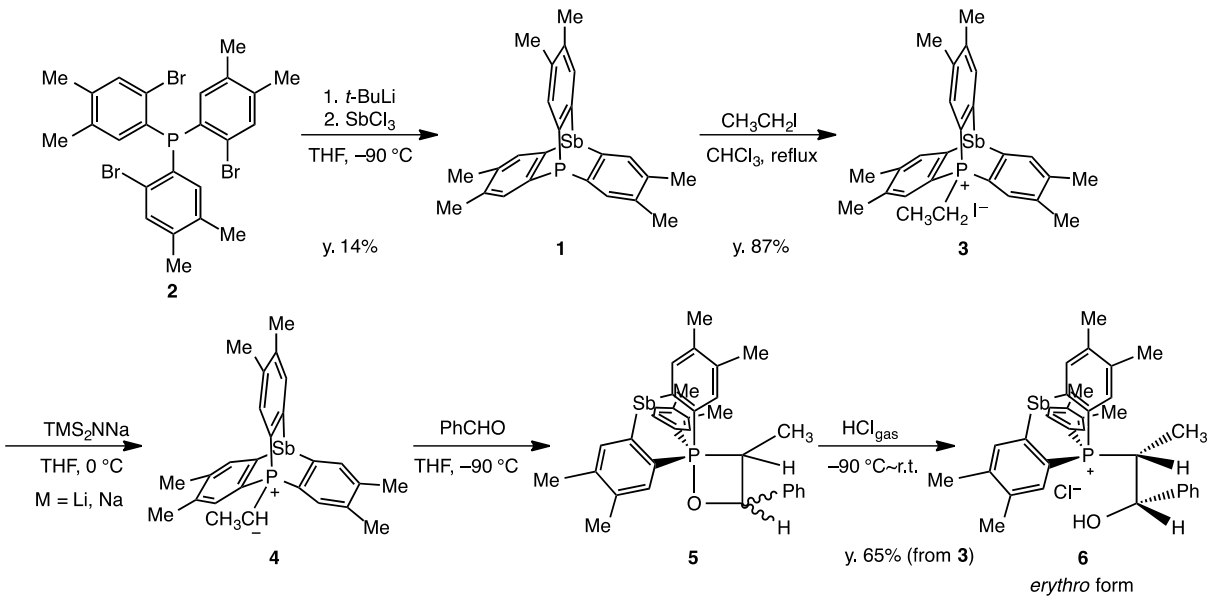
In this paper, we describe the (*E*)-selective Wittig reactions of a non-stabilized phosphonium ylide bearing a phosphastibatriptycene skeleton with benzaldehydes in the presence of lithium and sodium salts and to reveal the effect of a tridentate ligand on (*E*)-selective alkene formation. We will discuss the property of the intermediate, a 1,2-oxaphosphetane bearing a phosphastibatriptycene skeleton, comparing with the results of the triphenylphosphine system.

Results and Discussion

Generation of non-stabilized phosphonium ylides and preparation of the corresponding *β*-hydroxyalkylphosphonium salts

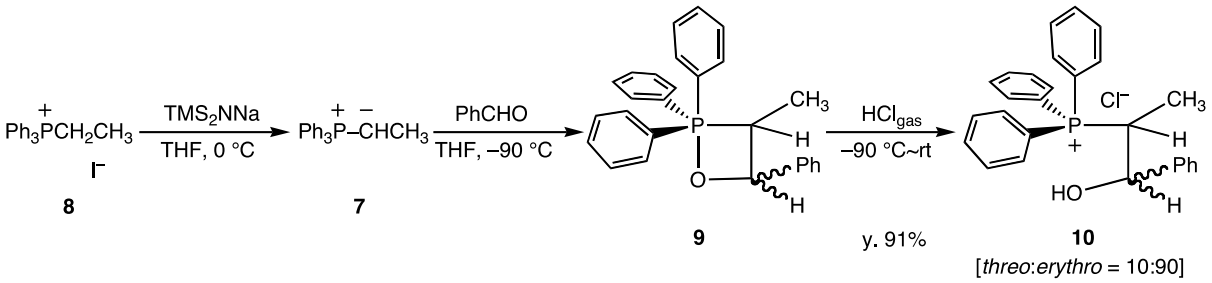
2,3,6,7,14,15-Hexamethylphosphastibatriptycene (**1**) was prepared in 14% yield by the revised method based on our previous one, namely, the reaction of tris(bromoaryl)phosphine **2** with *t*-BuLi, followed by the addition of antimony trichloride gave the crude product, which was purified by treatment with AcOEt/hexane and then with acetone (**Scheme 1**).[10,27] Phosphastibatriptycene **1** was reacted with ethyl iodide in $CHCl_3$ under reflux condition for 11 days to give the pure ethylphosphonium iodide **3** with ^{31}P chemical shift of 12.7 ppm in 87% yield by the filtration with THF.[28,29] The crystal structure of **3** was determined by X-ray

crystallography using the single crystals obtained from chlorobenzene as shown in Figure 1.[28] Yellow colored non-stabilized phosphonium ylide **4** was generated in THF by the reaction of **3** with TMS_2NLi or TMS_2NNa at 0 °C, giving a $^{31}P\{^1H\}$ NMR signal at 6.63 ppm in both cases. The ylide was reacted with benzaldehyde at –90 °C to give 1,2-oxaphosphetane **5** as an intermediate which was detected by VT-$^{31}P\{^1H\}$ NMR spectroscopy (the intermediates are discussed in details in the Wittig reaction section). To trap the intermediate, gaseous HCl generated from $NaCl–H_2SO_4$ was bubbled into the reaction mixture at –90 °C in Scheme 1. Consequently, *β*-hydroxyalkylphosphonium salt **6** was obtained in 54% yield after the purification by gel permeation chromatography (GPC). The mass spectrum performed by positive ESI showed *m/z* 599.1463, which was exactly in agreement with the calculated value for the molecular formula of *β*-hydroxyalkylphosphonium ion, $C_{33}H_{35}OPSb$, *m/z* 599.1458. In the $^{31}P\{^1H\}$ NMR spectrum of **6**, the signal of the phosphonium ion was observed at 18.2 ppm, which downfield shifted from that of ethylphosphonium iodide **3**. ^1H and $^{13}C\{^1H\}$ NMR spectra of **6** also showed the signals due to 1-hydroxy-1-phenyl-2-propyl and the phosphastibatriptycene moieties. We could not determine the stereochemistry around two carbons at *α*- and *β*-positions of the 1-hydroxy-1-phenyl-2-propyl group of **6** from these NMR spectral data. However, the stereochemistry of **6** was estimated to be the *erythro* form from the following discussion based on *β*-hydroxyalkylphosphonium salt bearing an ethoxycarbonyl group.[21,30,31]



Scheme 1

Triphenylphosphonium ylide **7** was prepared in a THF solution from ethyltriphenylphosphonium iodide **8** under the same reaction conditions as non-stabilized phosphonium ylide **4**. The reaction of **7** with benzaldehyde gave 1,2-oxaphosphetane **9**, which was observed at –62.3 ppm as only one signal by $^{31}P\{^{1}H\}$ NMR spectroscopy at –90 °C, similar to the *n*-propyl derivative observed at –61.9 ppm.[15] After its observation, gaseous HCl was added to the reaction mixture to provide *β*-hydroxyalkylphosphonium salts **10** in 91% yield as a mixture of *erythro*- and *threo*-forms in the ratio of 90:10 (**Scheme 2**). The signals at 30.9 ppm and 30.7 ppm were assigned to *erythro*- and *threo*-forms **10a** and **10b**, respectively, by comparison of their ^{31}P NMR chemical shifts with those (23.94 and 23.05 ppm in $CDCl_3$ at –35 °C[15]) of the reported *erythro*- and *threo*-(1-hydroxy-1-phenyl-2-propyl)triphenylphosphonium bromides and (31.4 and 31.0 ppm in $CDCl_3$ at room temperature[23]) of the reported *β*-hydroxyalkylphosphonium bromides bearing *o*-bromophenyl group at the *β*-position, respectively. The ^{1}H and ^{13}C NMR spectra also showed two sets of the triphenylphosphonio and 1-hydroxy-1phenyl-2-propyl moieties for *erythro*- and *threo*-forms **10a** and **10b**, which were similar to those of *β*-hydroxyalkylphosphonium bromides, as reported by Maryanoff *et al.* and Gilheany *et al.*[15,23]



Scheme 2

Structure of ethylphosphonium salt 3

Single crystals of ethylphosphonium salt **3** were obtained by slow evaporation of chlorobenzene and the X-ray crystallographic analysis showed *orthorhombic* as a crystal system and *P*bca as a space group (**Figure 1**).[32] The phosphorus atom has the P–C_{ethyl} bond, 1.780(4) Å, and three P–C bonds of the phosphastibatriptycene skeleton, 1.797(4), 1.803(4), and 1.804(4) Å, which are ca. 0.04 Å shorter than those of **1** due to the positively charged phosphorus. The average value (106.20°) of C–P–C angles of the phosphastibatriptycene skeleton of **3** is ca. 6° larger than that (100.07°) of **1** and ca. 6° smaller than that (112.56°) of

C–P–C angles with C1 of the ethyl group, indicating that all C–P–C angles of **3** are scattered within ca. ±3° comparing with the tetrahedral angle. On the other hand, the antimony atom of **3** has a pyramidal structure with incisive form to compare with that of **1**, as determined from the Sb–C bond lengths, 2.165(4), 2.172(4), 2.179(4) Å for **3** and 2.149(4), 2.151(5), 2.151(4) Å for **1**, and C–Sb–C bond angles, 89.27(14)°, 90.24(15)°, 89.43(15)° for **3**, and 90.0(2)°, 90.0(2)°, 90.8(2)° for **1**, although those largely do not affect the distance between phosphorus and antimony atoms in the skeleton. The X-ray analysis indicated the difference of the spatial distance of P···Sb between **1**, 3.482 Å, and **3**, 3.349 Å, is attributable to the structural change from pyramidal to tetrahedral phosphorus atom. The antimony atom at the opposite side of the phosphorus atom of **3** acts as a σ-donor, rather than a π-donor, because of its lone pair with high s-character and its low electronegativity (1.82), respectively.[33] Furthermore, it contributes to make the skeleton rigid. As for the reactivity of the antimony atom, since the Sb–C bonds of the phosphastibatriptycene skeleton were easily cleaved by *n*-BuLi, we used lithium and sodium bistrimethylsilylamides as bases in the following Wittig reactions to estimate the yields and observe intermediates by VT-NMR spectroscopy.[34]

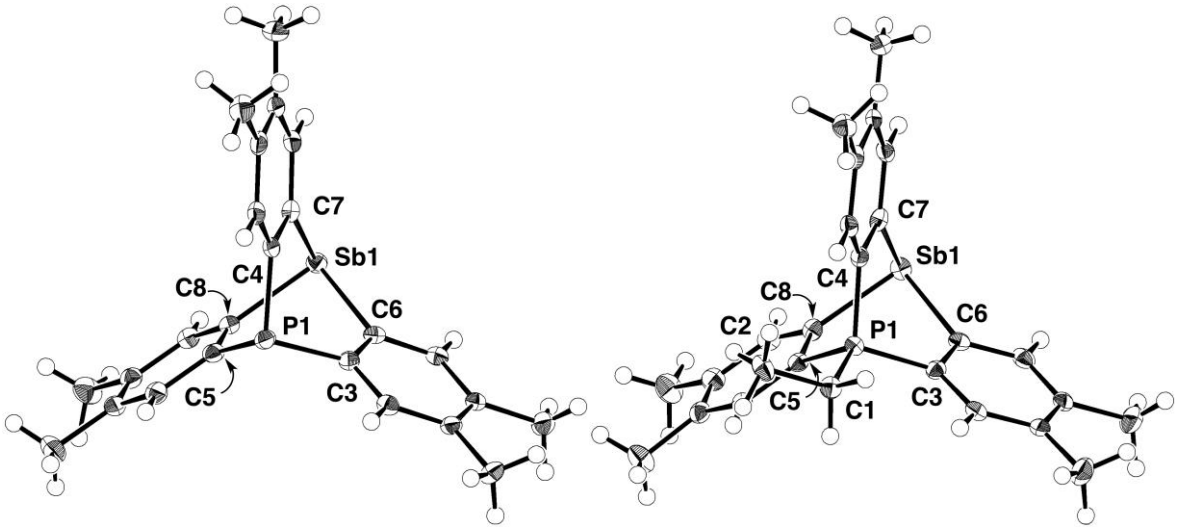


Figure 1: ORTEP drawings of phosphastibatriptycene **1** and ethylphosphonium iodide **3**. The counter anion, I⁻ of **3** was omitted for clarity. Selected bond lengths (**Å**) and angles (deg) for **1**; P1–C3: 1.844(5), P1–C4: 1.844(5), P1–C5: 1.849(5), Sb1–C6: 2.149(4), Sb1–C7: 2.151(5), Sb1–C8: 2.151(4), P···Sb: 3.482, C3–P1–C4: 100.2(2), C3–P1–C5: 100.6(2), C4–P1–C5: 99.4(2), C6–Sb1–C7: 90.0(2), C6–Sb1–C8: 90.0(2), C7–Sb1–C8: 90.8(2), **3**; P1–C1: 1.780(4), P1–C3: 1.797(4), P1–C4: 1.803(4), P1–C5: 1.804(4), Sb1–C6: 2.165(4), Sb1–C7: 2.172(4), Sb1–C8: 2.179(4), C1–C2: 1.539(5), P···Sb: 3.349, C1–P1–C3: 112.42(18), C1–

P1–C4: 112.11(18), C1–P1–C5: 113.15(18), C3–P1–C4: 107.06(18), C3–P1–C5: 107.49(18), C4–P1–C5: 104.06(18), C6–Sb1–C7: 89.27(14), C6–Sb1–C8: 90.24(15), C7–Sb1–C8: 89.43(15), C2–C1–P1: 116.3(3).

Wittig reactions of non-stabilized phosphonium ylides with benzaldehydes

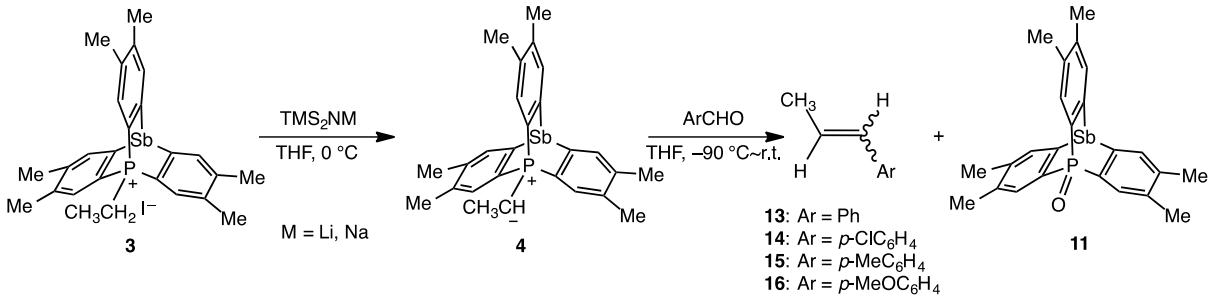
Reactions of non-stabilized phosphonium ylides **4** and **7** with benzaldehydes were conducted in THF at –90 °C in a sealed NMR tube with a screw valve to compare (*E*)- and (*Z*)-selectivity in the cases of a tridentate ligand and a monodentate ligand. When the reaction mixtures were allowed to warm from –90 °C to 25 °C for 2.5 h, NMR signals due to alkenes **13-16**[35-38] and phosphine oxides **11** or **12** were observed and the ratio of (*E*)- and (*Z*)-alkenes was recorded by ^{1}H NMR spectroscopy after 16 h to examine whether isomerization of the alkenes occurred under the reaction conditions or not (**Scheme 3**, **4**, and **Table 1**, **2**).

The reactions of ylide **4** bearing a phosphastibatriptycene skeleton with four benzaldehydes, PhCHO, *p*-ClC_6H_4CHO, *p*-MeC_6H_4CHO, and *p*-$MeOC_6H_4CHO$, showed the (*E*)-selective alkene formation in the ratios of 97:3, 75:25, 91:9, and 90:10 in the presence of lithium salt in Entries 1-4 whereas those of triphenylphosphonium ylide **7** gave (*E*)- and (*Z*)-alkenes **13-16** in the ratio of 31:69, 21:79, 49:51, 72:28 in Entries 5-8, which were dependent on the substituents at the *para*-position of benzaldehydes (**Table 1**). The substituent effect of the *para*-position on benzaldehydes in the triphenylphosphonium ylide system was much more than that in tridentate ligand system. In the latter system, the ratio of (*E*)- to (*Z*)-alkenes increases with an increase in electron-donating properties of the *para*-substituents.

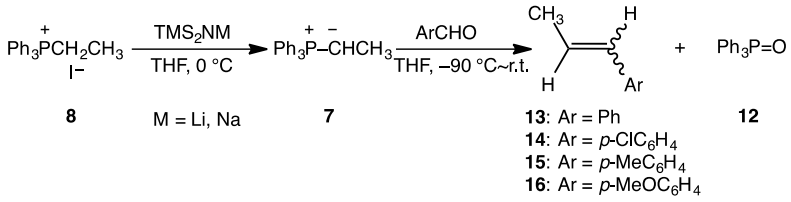
On the other hand, when the reactions in the presence of sodium salt were conducted, the alkenes **13-16** were obtained in the ratios of 87:13, 88:12, 80:20, 95:5 in Entries 1-4 and 22:78, 22:78, 25:75, 28:72 in Entries 5-8 in the reactions using non-stabilized phosphonium ylides **4** and **7**, respectively (**Table 2**). In both cases, almost no substituent effect of the *para*-position on benzaldehydes was observed, although the selectivity was completely different to each other.

The (*E*)-selectivity observed when using ylide **4** can be explained as follows. The equilibrium between the 1,2-oxaphosphetane and a mixture of the corresponding ylide and the aldehyde seems lying toward the latter, because the cation center of the ylide is stabilized by the inductive effect of electropositive antimony[33] as estimated from ^{31}P chemical shift of ylide **4**, 6.63 ppm in THF. Therefore, the (*E*)-alkenes are considered to have mainly formed by

thermodynamic control. In the case of the reaction using less stable ylide **7** with 13.5 ppm in THF, the stability of the aldehyde seems to contribute to the equilibrium more than that of the ylide, so that it is reasonable that (*E*)-selectivity increased with an increase in the stability of the aldehyde. Conclusively, in the presence of both lithium and sodium salts, (*E*)-selectivity and (*Z*)-selectivity in the reactions using ylides **4** and **7** were considered to result from thermodynamic and kinetic control, respectively.



Scheme 3



Scheme 4

Table 1: Yields and (*E*):(*Z*) ratios of alkenes for the Wittig reactions in the presence of Li salt[a]

Entry	Ylide	ArCHO	Alkene	Yield	(*E*):(*Z*) ratio
1	**4**	Ph	**13**	58%	97:3
2	**4**	*p*-ClC_6H_4	**14**	36%	75:25
3	**4**	*p*-MeC_6H_4	**15**	49%	91:9
4	**4**	*p*-$MeOC_6H_4$	**16**	55%	90:10
5	**7**	Ph	**13**	77%	31:69
6	**7**	*p*-ClC_6H_4	**14**	76%	21:79
7	**7**	*p*-MeC_6H_4	**15**	99%	49:51
8	**7**	*p*-$MeOC_6H_4$	**16**	91%	72:28

a) TMS_2NLi was used as base to generate ylides **4** and **7**.

Table 2: Yields and (*E*):(*Z*) ratios of alkenes for the Wittig reactions in the presence of Na salt[a]

Entry	Ylide	ArCHO	Alkene	Yield	(*E*):(*Z*) ratio
1	**4**	Ph	**13**	87%	87:13
2	**4**	*p*-ClC_6H_4	**14**	77%	88:12

3	**4**	*p*-MeC_6H_4	**15**	45%	80:20
4	**4**	*p*-$MeOC_6H_4$	**16**	49%	95:5
5	**7**	Ph	**13**	87%	22:78
6	**7**	*p*-ClC_6H_4	**14**	90%	22:78
7	**7**	*p*-MeC_6H_4	**15**	75%	25:75
8	**7**	*p*-$MeOC_6H_4$	**16**	99%	28:72

a) TMS_2NNa was used as base to generate ylides **4** and **7**.

Monitoring the Wittig reaction by VT-$^{31}P\{^1H\}$ NMR spectroscopy

In order to reveal the (*E*)-selective Wittig reaction of non-stabilized phosphonium ylide **4** bearing a phosphastibatriptycene skeleton with benzaldehydes, VT-$^{31}P\{^1H\}$ NMR spectra were recorded at 10 °C intervals from –90 °C to 25 °C as shown in Figures 2 and 3. The observation field was focused on the region from 40 to –100 ppm.

The NMR signal due to the intermediate of the Wittig reaction of non-stabilized phosphonium ylide **4**, which was prepared by deprotonation of ethylphosphonium iodide **3** with TMS_2NLi, with benzaldehyde in THF was observed at –57.3 ppm as a broad singlet at –80 °C, as shown in Figure 2. The broad signal observed at –57.3 ppm constantly shifted low field from –90 °C to –40 °C and the new signal was observed at –54.5 ppm. The phenomenon was also observed when TMS_2NNa was used as shown in Figure 3, although the chemical shifts (–57.3 and –55.2 ppm) and shape of the signals were different from those observed in the presence of lithium salt. The new signal at –55.2 ppm appeared at –40 °C and increased until –10 °C, while the signal at –57.3 ppm gradually increased from –90 °C to –40 °C, and then decreased from –40 °C to –20 °C, suggesting that isomerization of the first formed intermediate to another one started from –40 °C. When the temperature of the VT-experiment was cooled again after observation of two signals at –20 °C, the ratio of the signals did not change from –20 °C until –90 °C (see Figure 57 in supporting information), indicating the observed intermediate at –55.2 ppm was more thermodynamically stable than the first formed one. The signal assigned to phosphine oxide **11** was observed at 22.0 ppm from –20 °C to 25 °C. The results showed that the signals observed at –57.3 ppm from –90 °C to –10 °C and at –55.2 ppm from –40 to 0 °C, respectively, should be assigned to the different structural intermediates giving the corresponding phosphine oxide and alkenes. Two other signals were detected at 6.63 and –12.0 ppm during the VT-$^{31}P\{^1H\}$ NMR experiments. The signal at –12.0 ppm is assigned to the parent phosphastibatriptycene, while the signal at 6.63 ppm is due to non-stabilized phosphonium ylide **4** (see Figures 15, 16 in supporting information)

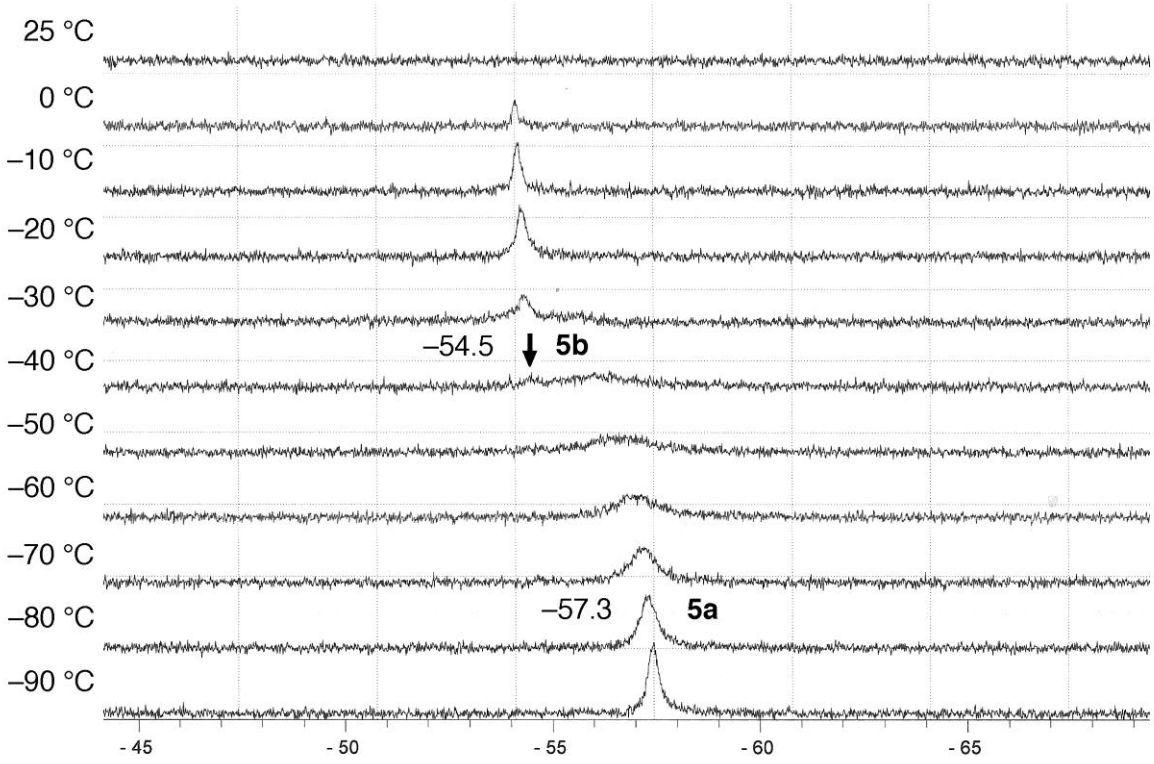


Figure 2. VT-$^{31}P\{^{1}H\}$ NMR spectra of the reaction of **4** with PhCHO in the presence of Li salt

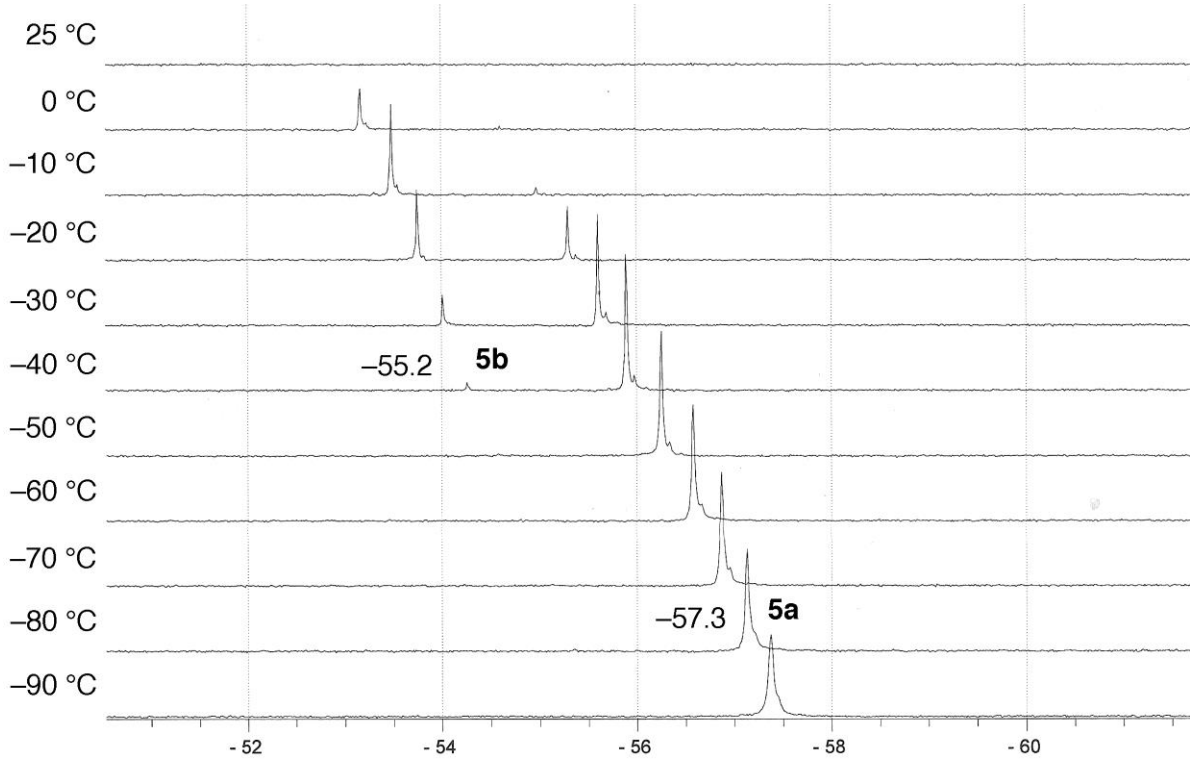
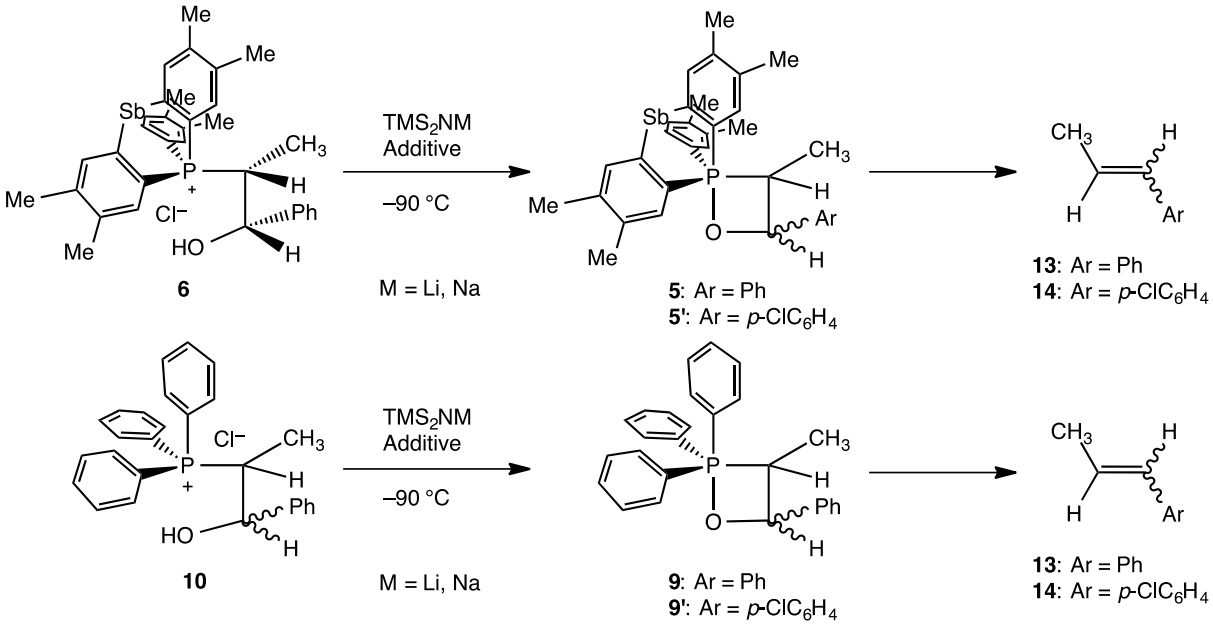


Figure 3. VT-$^{31}P\{^{1}H\}$ NMR spectra of the reaction of **4** with PhCHO in the presence of Na

salt



Scheme 5

Table 3: Yields and (*E*):(*Z*) ratios of alkenes for deprotonations in the presence of Li and Na salts

Entry	*β*-OH	M	Additive	Time, Temp.	Yield ((*E*):(*Z*) ratio) for **13**	Yield ((*E*):(*Z*) ratio) for **14**
1	**6**	Li	none	5 min, –40 °C	42% (70:30)	-
2	**6**	Li	*p*-ClC$_6$H$_4$CHO	1 h, –40 °C	23% (99:1)	38% (99:1)
3	**6**	Na	none	5 min, –40 °C	63% (15:85)	-
4	**6**	Na	none	1 h, –40 °C	28% (69:31)	-
5	**6**	Na	*p*-ClC$_6$H$_4$CHO	5 min, –40 °C	18% (22:78)	14% (78:22)
6	**6**	Na	*p*-ClC$_6$H$_4$CHO	1 h, –40 °C	8% (0:100)	76% (77:23)
7	**10**	Na	none	5 min, 0 °C	37% (28:72)	-
8	**10**	Na	PhCHO	5 min, 0 °C	82% (27:73)	-
9	**10**	Na	*p*-ClC$_6$H$_4$CHO	5 min, 0 °C	52% (26:74)	9% (0/100)

Deprotonation of *β*-hydroxyalkylphosphonium salt **6** with TMS$_2$NLi at –40 °C for 5 minutes gave (*E*)- and (*Z*)-alkenes in the ratio of 70:30 in the VT-NMR measurement (Entry 1, **Table 3**). The reaction gave mainly (*E*)-alkene, although the ratio of (*Z*)-alkene was larger than that (97:3) of the Wittig reaction (Entry 1, **Table 1**). On the other hand, the deprotonation of **6** with TMS$_2$NNa gave (*E*)- and (*Z*)-alkenes in the ratio of 15:85 (Entry 3, **Table 3**), which was different result from that (87:13) of the Wittig reaction of non-stabilized phosphonium ylide **4** with benzaldehyde (Entry 1, **Table 2**). The ratio of 15:85 was obtained after keeping the reaction mixture at –40 °C for 5 min in the VT-NMR measurement (Entry 3,

Table 3), while the ratio became 69:31 after allowing to stand for 1 h at –40 °C in another measurement (Entry 4, **Table 3**). The results showed that deprotonation of **6** in the presence of lithium salt gave more easily (*E*)-alkene than that in the presence of sodium salt.

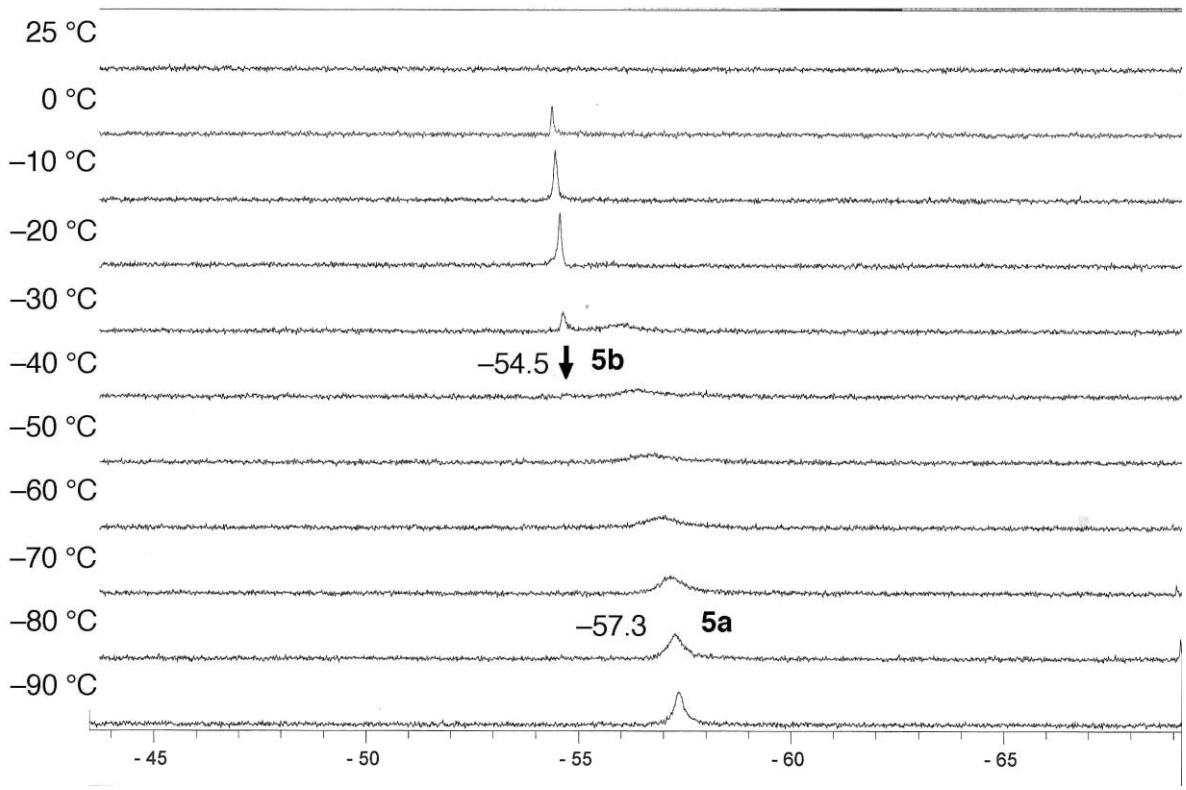


Figure 4. VT-$^{31}P\{^{1}H\}$ NMR spectra of the reaction of *β*-hydroxyalkylphosphonium salt **6** with TMS_2NLi

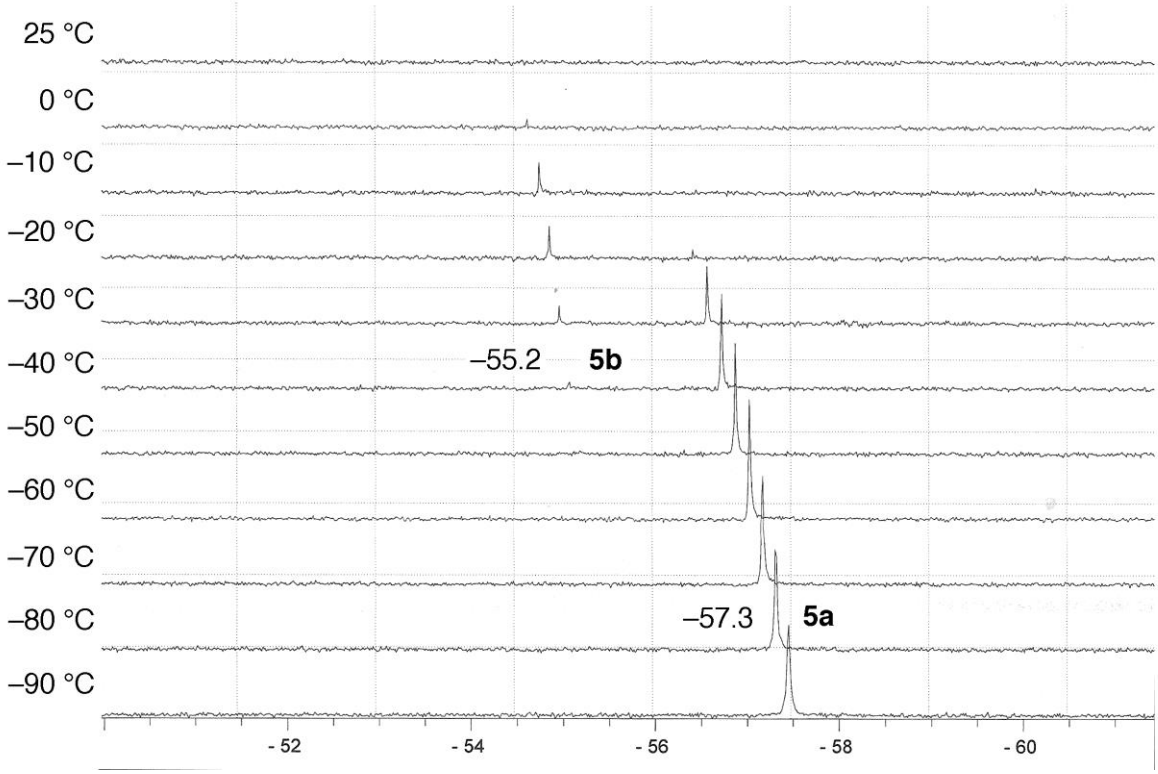
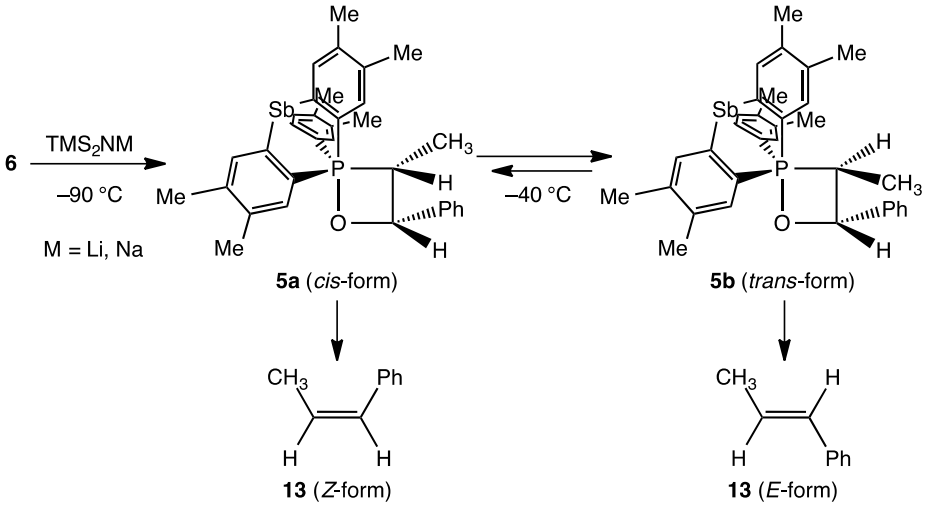


Figure 5. VT-$^{31}P\{^{1}H\}$ NMR spectra of the reaction of *β*-hydroxyalkylphosphonium salt **6** with TMS_2NNa

VT-$^{31}P\{^{1}H\}$ NMR spectra of the deprotonation of **6** with TMS_2NLi showed only one signal was observed at –57.3 ppm at –80 °C and then new signal appeared at –54.5 ppm from –40 °C, whereas two signals were observed at –57.3 ppm and –55.2 ppm in the presence of sodium salt, similar to the Wittig reaction of non-stabilized phosphonium ylide **4** with benzaldehyde (**Scheme 5**, **Table 3**, and **Figures 4** and **5**). The results indicated that these two signals were due to *cis*- and *trans*-1,2-oxaphosphetanes **5**. Phosphine oxide **11**, non-stabilized phosphonium ylide **4**, and phosphastibatriptycene **1** were observed at 22.0 ppm, 6.63 ppm, and –12.0 ppm, respectively, together with other unclear signals by VT-$^{31}P\{^{1}H\}$ NMR spectroscopy (see Figures 18, 19 in supporting information).

Alkene formation by deprotonations of **6** and VT-experiments suggested that the initial intermediate observed at –80 °C was *cis*-1,2-oxaphosphetane **5a** and the later one at –40 °C was *trans*-form **5b** because *cis*-form was directly formed from the deprotonation of **6**, decomposed to give (*Z*)-alkene with retention of the configuration, and isomerized to a thermodynamically stable isomer, *trans*-form **5b** (Scheme 6). Namely, the *cis*-form was selectively formed as a kinetic product in the Wittig reaction of the ylide bearing a phosphastibatriptycene skeleton and the *trans*-form was produced as the thermodynamically stable isomer in the equilibrium between the intermediates. The thermodynamic stability of

the two isomers was also investigated in the VT-experiments by re-cooling the two intermediates in the Wittig reaction of **4** and PhCHO in the presence of sodium salt (see Figure 57 in supporting information). The signals observed at –20 °C assigned to two intermediates did not change when these were observed at –90 °C again, showing that *trans*-form **5b** was thermodynamically more stable than *cis*-form **5a**. Isomerization occurred at the same temperature (–40 °C) in the presence of both lithium and sodium salts, but the process was faster with lithium salt (Entries 1 and 3, **Table 3**) because it assisted isomerization by coordinating with the oxygen atom of *cis*-1,2-oxaphosphetane **5a**. The corresponding Li-betaine was observed at 19.2 ppm as a broad signal together with the broad signal of *cis*-form **5a** until –40 °C, suggesting the equilibrium between Li-betaine and 1,2-oxaphosphetane (see Figure 18 in supporting information). On the other hand, the equilibrium between a betaine and 1,2-oxaphosphetane was not observed in the presence of sodium salt even though the isomerization from *cis*-form **5a** to *trans*-form **5b** was observed at the same temperature, –40 °C, of that in the presence of lithium salt. The result in the presence of sodium salt did not clearly show that the isomerization proceeded via a betaine intermediate or by retro-[2+2] cycloaddition.



Scheme 6

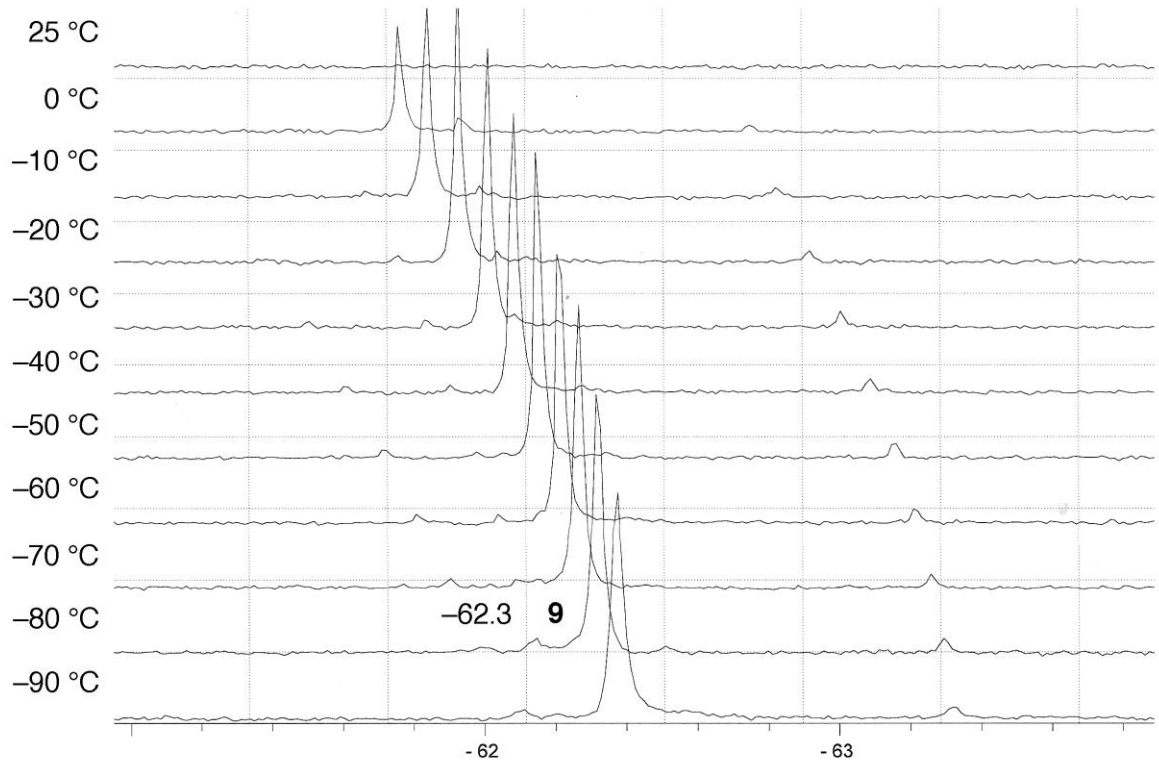


Figure 6. VT-$^{31}P\{^1H\}$ NMR spectra of the reaction of Ph_3P=CHMe(**7**) with PhCHO in the presence of Na salt

The $^{31}P\{^1H\}$ NMR spectrum at –80 °C of the reaction mixture of triphenylphosphonium ylide **7** showed only one signal at –62.3 ppm, which was assigned to 1,2-oxaphosphetane **9** by comparing with the result of the isolation of *β*-hydroxyalkylphosphonium salts **10** followed by deprotonation with TMS_2NNa (**Figure 6**). In contrast to the result of the phosphastibatriptycene system, the observed signal gradually increased from –90 °C to –40 °C and then decreased from –40 °C to –10 °C without any new signal appearing, suggesting that intermediate **9** already formed at –90 °C and was stable even at –40 °C. *β*-Hydroxyalkylphosphonium salts **10** were obtained as a diastereomeric mixture of *threo*- and *erythro*-forms in the ratio of 10:90 estimated by integral value in the ^1H NMR spectrum (**Scheme 2**). The fact that the product ratios were 28:72 (Entry 7, **Table 3**) and 22:78 (Entry 5, **Table 2**) in the deprotonation of **10** and in the Wittig reaction of **7** with benzaldehyde, respectively, means that the stereochemical drift occurred in both reactions, judging from that their ratios were different from 10:90 expected from both the ratio of the starting *threo*- and *erythro*-**10** and the ratio of intermediates just before quenching with HCl to give **10** in Entry 7 (**Scheme 5**, **Table 3**). Although the signals due to *cis*- and *trans*-1,2-oxaphosphetanes **9** should be observed during the VT measurement, they were not clearly observed. Therefore, it is considered that the signal overridden another one assigned

to other isomer or that another signal was too small to be observed as same as the reported results of the reaction using the triphenylphosphonium ylide.[15)]

P–H and H–H coupling constants to characterize *cis*- and *trans*-1,2-oxaphosphetanes 5

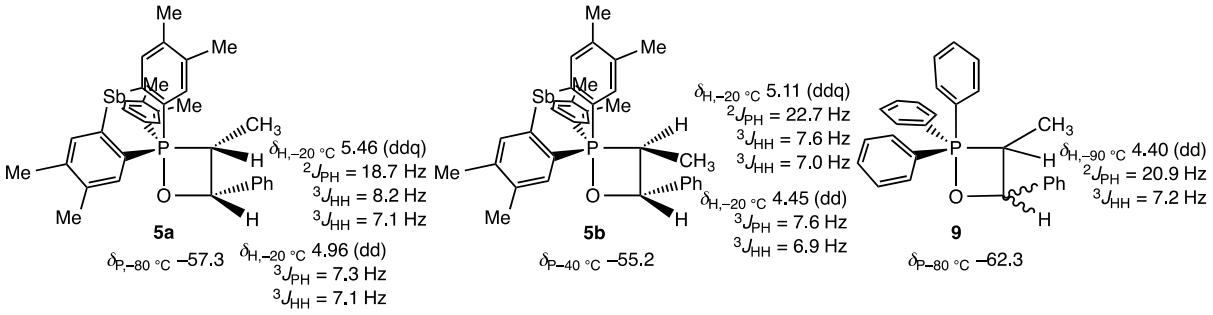


Figure 6

Figure 7. Assignment of 1,2-oxaphosphetane **5a**, **5b**, and **9**

The P–H and H–H coupling constants were estimated by ^{1}H NMR spectroscopy in order to assign the signals observed at –57.3 and –55.2 ppm in ^{31}P{^{1}H} NMR spectra to 1,2-oxaphosphetanes **5a** and **5b** (**Figure 7** and Figures 26-29 in supporting information). The ^{1}H NMR spectra were recorded at each temperature with the ^{31}P{^{1}H} NMR spectra to analyze P–H and H–H coupling constants. The P–H and H–H coupling constants were estimated in ^{1}H NMR spectra at –20 °C and –10 °C after checking that the target intermediates were observed at –57.3 and –55.2 ppm in ^{31}P{^{1}H} NMR spectra. The proton decoupling technique was used to examine the H–H coupling constants. In ^{1}H NMR spectra at –20 °C and –10 °C, we focused on signals due to methine protons at the 3- and 4-positions of 1,2-oxaphosphetanes **5**. The proton signals at 5.46 and 4.95 ppm and at 5.11 and 4.45 ppm corresponding to the signals at –57.3 and –55.2 ppm in ^{31}P{^{1}H} NMR spectra, respectively, were assigned to methine protons at the 3- and 4-positions of 1,2-oxaphosphetanes **5a** and **5b**, respectively. The signal at 5.46 ppm showed double of doublet of quartet with $^{2}J_{PH}$ = 18.7 Hz, $^{3}J_{HH}$ = 7.1 Hz, and $^{3}J_{HH}$ = 8.2 Hz and the signal at 4.95 ppm had double of doublet with $^{4}J_{PH}$ = 7.3 Hz and $^{3}J_{HH}$ = 7.1 Hz, which were assigned to the methine protons at 3- and 4-positions of one isomer, respectively. Similarly, the signal at 5.11 ppm showed double of double of quartet with $^{2}J_{PH}$ = 22.7 Hz, $^{3}J_{HH}$ = 7.6 Hz, and $^{3}J_{HH}$ = 7.0 Hz, and the signal at 4.45 ppm had double of doublet with $^{4}J_{PH}$ = 7.6 Hz and $^{3}J_{HH}$ = 6.9 Hz, which are due to the methine protons at the 3- and 4-positions of another isomer, respectively. The methyl proton signals were not detected due to being behind THF signals as a solvent. The observed $^{2}J_{PH}$ coupling constants, 18.7 Hz and 22.7 Hz were similar to

those of the reported for *O*-apical 1,2-oxaphosphetanes, $^{2}J_{PH}$ = 20.0, 23.0 Hz, and *N*-apical 1,2-azaphosphetidines, $^{2}J_{PH}$ = 19.6, 21.6 Hz, bearing the Martin ligand, showing that the 1,2-oxaphosphetanes **5a** and **5b** had the *O*-apical forms because both the P–H coupling constants were much larger than those of the reported for *C*-apical forms, which are $^{2}J_{PH}$ = 6.8, 11.2 Hz for the reported 1,2-oxaphosphetane and $^{2}J_{PH}$ = 5.6, 7.9 Hz for the reported 1,2-azaphosphetidine.[39,40] The H–H coupling constants between the 3- and 4-methine protons were 7.1 Hz for 4.95 and 5.46 ppm and 6.9 Hz and 7.0 Hz (averaged value is 7.0 Hz) for 4.45 and 5.11 ppm. This confirmed that the former was the *cis*-form and the latter was the *trans*-form, because in 3-methyl-2-phenyloxetanes, the *cis*-form has a larger coupling constant ($^{3}J_{HH}$ = 8.1 Hz) than that ($^{3}J_{HH}$ = 6.7 Hz) of the *trans*-form,[41] and the reported 1,2-oxaphosphethanes have similar tendencies, that is, $^{3}J_{HH}$ = 7.5 Hz for *cis*-form and $^{3}J_{HH}$ = 5.9 Hz for *trans*-form.[15] From these results, the two signals observed at –57.3 and –55.2 ppm in $^{31}P\{^{1}H\}$ NMR spectra were assigned to *cis*- and *trans*-1,2-oxaphosphetanes **5a** and **5b**, respectively. The proton signal at the 3-position of 1,2-oxaphosphetane **9** in the reaction of triphenylphosphonium ylide **7** with benzaldehyde showed double of quartet with $^{2}J_{PH}$ = 20.9 Hz and $^{3}J_{HH}$ = 7.2 Hz for the methyl group, while the coupling constant between the 3- and 4-positions was not observed due to overlapping with the observed signals. The observed 1,2-oxaphosphetane **9** in the NMR spectra was considered to have an *O*-apical form according to above aspect and a *cis*-form judging from the (*Z*)-selectivity (**Figure 7** and Figures 30, 31 in supporting information).

Crossover experiments using *β*-hydroxyalkylphosphonium salts 6 and 10 in the presence of *p*-chlorobenzaldehyde

The VT-$^{31}P\{^{1}H\}$ NMR spectra of the reactions of non-stabilized phosphonium ylides **4** and **7** with *p*-chlorobenzaldehyde in the presence of sodium salt were measured before conducting the crossover experiments (**Scheme 5**, **Table 3**, **Figures 8**, **9**, and Figures 20, 24 in supporting information). In the phosphastibatriptycene skeleton system, two signals at –57.2 ppm and –54.8 ppm at –80 °C and –40 °C were observed as the intermediates, respectively, although the chemical shifts were downfield of those for the benzaldehyde derivatives due to the electro-withdrawing Cl group at the *para*-position. In the triphenyl derivative, only one signal was observed at –61.6 ppm at –80 °C as the intermediate, which was also shifted downfield compared with that of the benzaldehyde derivative, –62.3 ppm.

Crossover experiments were performed by deprotonation of *β*-hydroxyalkylphosphonium salts **6** and **10** with TMS_2NNa in the presence of ca. 2

equivalents of *p*-chlorobenzaldehyde at –90 °C. The VT-$^{31}P\{^{1}H\}$ NMR spectra were recorded from –90 °C to 25 °C. Only one signal (–56.6 ppm) due to *cis*-4-phenyl-1,2-oxaphosphetane **5a** was initially observed at –90 °C, and then from at –50 °C to –40 °C, two signals were observed at –56.6 and –56.5 ppm, indicating the equilibration between **5a** and *cis*-4-*p*-chlorophenyl-1,2-oxaphosphetane **5a'**. At –40 °C, two sets of two signals were observed at –56.6 and –55.2 ppm and at –56.5 and –54.6 ppm, which were assigned to *cis*- and *trans*-4-phenyl-1,2-oxaphosphetanes **5a** and **5b** and *cis*- and *trans*-4-*p*-chlorophenyl-1,2-oxaphosphetanes **5a'** and **5b'**, respectively. These results demonstrated that equilibration between the phenyl- and *p*-chlorophenyl derivatives and between *cis*- and *trans*-forms occurred almost simultaneously.

Under the conditions for 5 min at –40 °C, phenyl- and *p*-chlorophenylalkenes **13** and **14** were obtained with (*E*):(*Z*) ratios of 22:78 in 18% yield and 78:22 in 14% yield, respectively, while the total yield was lower than the other entries because the extrusion of aldehydes from *cis*-forms **5a** and **5a'** and the formation of *trans*-forms **5b** and **5b'** had the different rates between the phenyl and *p*-chlorophenyl 1,2-oxaphophetanes under the conditions in Entry 5 (**Scheme 5**, **Table 3**). The product ratio between **13** and **14** was changed to be 8% (0:100) and 76% (77:23) under the condition for 1 hour at –40 °C, supporting that the exchange from benzaldehyde to *p*-chlorobenzaldehyde moieties occurred under the conditions to give more stable 1,2-oxaphosphetane in Entry 6 (**Scheme 5**, **Table 3**). The major products were *Z*-form for **13** and *E*-form for **14** because the phenyl derivative was produced with retention of the stereochemistry from the starting phosphonium salt **6** and while the *p*-chlorophenyl derivative was formed as a thermodynamically stable product.

On the other hand, two signals were observed at –61.8 and –61.0 ppm for phenyl and *p*-chlorophenyl derivatives **9** and **9'** at 0 °C, respectively, by the VT-NMR measurements from –90 to 25 °C. Deprotonation of **10** provided **13** in 52% yield with the (*E*):(*Z*) ratio of 26:74 and **14** in 9% yield with the (*E*):(*Z*) ratio of 0:100 in Entry 9 (**Scheme 5**, **Table 3**). Although the equilibrium between *cis*- and *trans*-forms was not clearly observed, the ratio of the (*E*):(*Z*)-alkenes with the phenyl group was 26:74, which showed the stereochemical drift from that (10:90) of *threo*- and *erythro*-*β*-hydroxyalkylphosphonium salts **10** even in the presence of *p*-chlorobenzaldehyde. The product yield in deprotonation of **10** increased from 37% to 82% by adding benzaldehyde in Entries 7 and 8 (**Table 3**), indicating the existence of the reversible process between 1,2-oxaphosphetane **9** and non-stabilized phosphonium ylide-benzaldehyde even though in the triphenyl system.

The above results indicated that benzaldehyde was exchanged with

p-chlorobenzaldehyde at –50 to –40 °C for the phosphastibatriptycene derivative and at around 0 °C for the triphenyl system. In VT-^{1}H NMR spectra, the signals due to benzaldehyde were observed at –40 °C in the deprotonation of *β*-hydroxyalkylphosphonium salts **6** with TMS_2NNa, indicating that the extrusion of benzaldehyde from 1,2-oxaphosphetane **5** occurred. Similarly, the deprotonation of **6** with TMS_2NLi in the presence of *p*-chlorobenzaldehyde gave (*E*)- and (*Z*)-*p*-chlorophenylalkenes **14** in 25% together with benzaldehyde (Entry 2, **Table 3**), showing that benzaldehyde was extruded from **6** in the deprotonation, inducing the formation of **14** in a similar fashion to when TMS_2NNa was used. The results of the crossover experiments strongly suggested that the equilibrium between 1,2-oxaphosphetane **5** and non-stabilized phosphonium ylide **4**–benzaldehyde induced the isomerization shown in Scheme 6 from *cis*-form **5a** to *trans*-form **5b** in the presence of lithium and sodium salts as shown mechanism in Scheme 7.

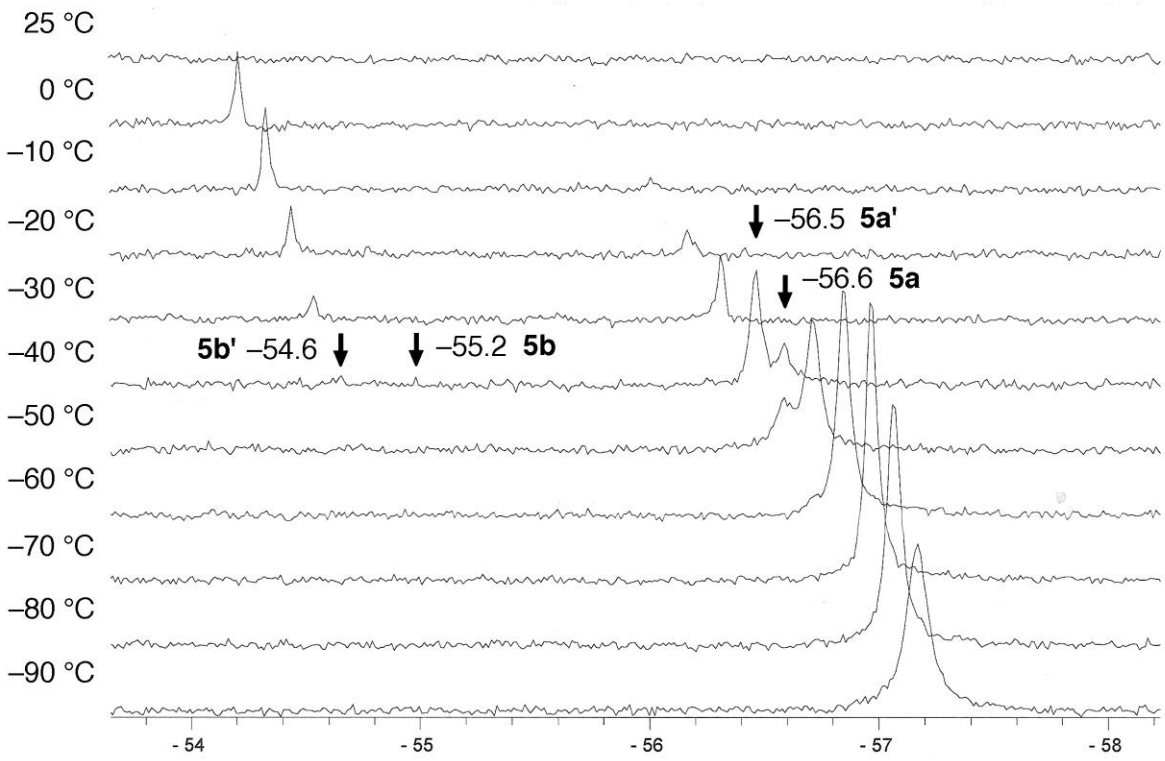


Figure 8. VT-$^{31}P\{^1H\}$ NMR spectra of the reaction of *β*-hydroxyalkylphosphonium salt **6** with TMS_2NNa in the presence of *p*-ClC_6H_4CHO.

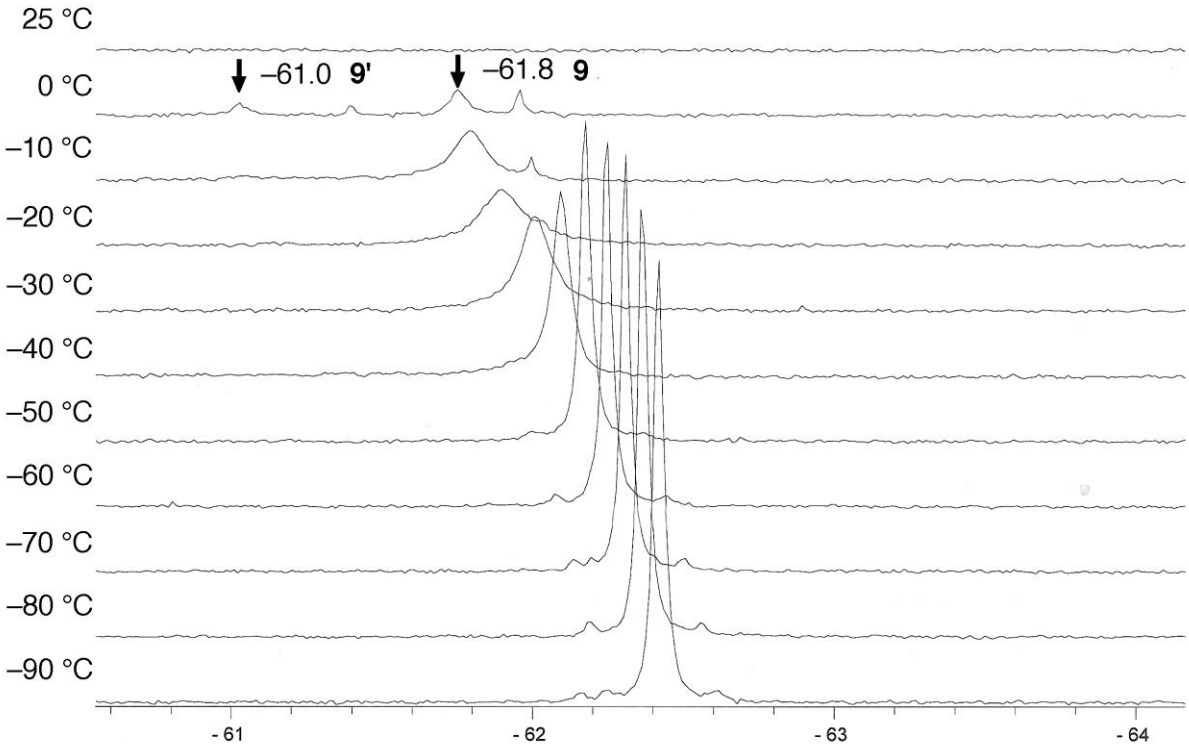


Figure 9. VT-$^{31}P\{^{1}H\}$ NMR spectra of the reaction of *β*-hydroxyalkylphosphonium salt **10** with TMS_2NNa in the presence of *p*-ClC_6H_4CHO

Calculations to estimate free energies and ^{31}P NMR chemical shifts of intermediates

1,2-Oxaphosphetanes with a methyl group at the 3-position and a phenyl group at the 4-position were calculated by density functionalized theory method (DFT) to estimate the optimized structures and their free energies.[42] The *trans*-forms, **17b** and **9b**, were 2.24 and 1.74 kcal/mol more stable than the *cis*-forms, **17a** and **9a**, respectively, which are in good agreement with the reported 1,2-oxaphosphetanes.[5] The orientation of the aryl group can be recognized as the only difference between the structures of the two 1,2-oxaphosphetanes bearing a phosphastibatriptycene skeleton and triphenylphosphine moiety. That is, the P–C bonds of the aryl group and the methyl group in phosphastibatriptycene system were perpendicular, as opposed to being parallel in the triphenylphosphine system to avoid steric repulsion. Since the repulsion in the phosphastibatriptycene system was larger than that of the triphenylphosphine system, the dihedral angles of P–C3–C4–O of *trans*- and *cis*-forms in the phosphastibatriptycene system were smaller than those of the triphenylphosphine system and the sums of inner angles of the 1,2-oxaphosphetane ring in the former system was larger than in the latter. Ring strain in 1,2-oxaphosphetanes bearing the phosphastibatriptycene system was expected to be larger than in those bearing the triphenylphosphine moiety,

meaning that conversion back to the starting materials occurred more readily in the former system than the latter. The calculated results suggested that the observed phenomenon in VT-$^{31}P\{^{1}H\}$ NMR of 1,2-oxaphosphetane **5** bearing the phosphastibatriptycene skeleton was caused by the isomerization at –40 °C from kinetic product, *cis*-form **5a**, to thermodynamically stable *trans*-form **5b** through the equilibrium between the corresponding 1,2-oxaphosphetane and phosphonium ylide–aldehyde mixture. Moreover, the observed chemical shifts in $^{31}P\{^{1}H\}$ NMR showed at –56.6 for *cis*-form **5a** and –55.2 for *trans*-form **5b**, respectively, whose trend was in consistent with that of the calculated ones at –48.7 ppm for *cis*-form **17a** and –46.1 ppm for *trans*-form **17b** based on H_3PO_4 (**Figure 10**, **Table 4**).

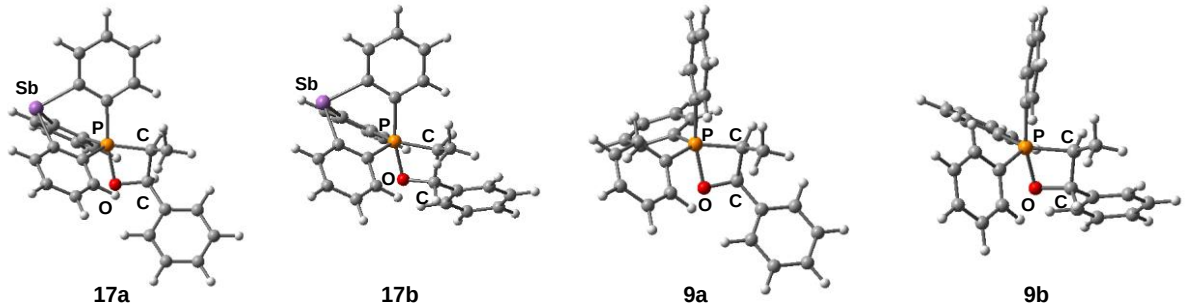


Figure 10: Optimized structures of 1,2-oxaphosphetanes bearing phosphastibatriptycene and triphenyl moieties

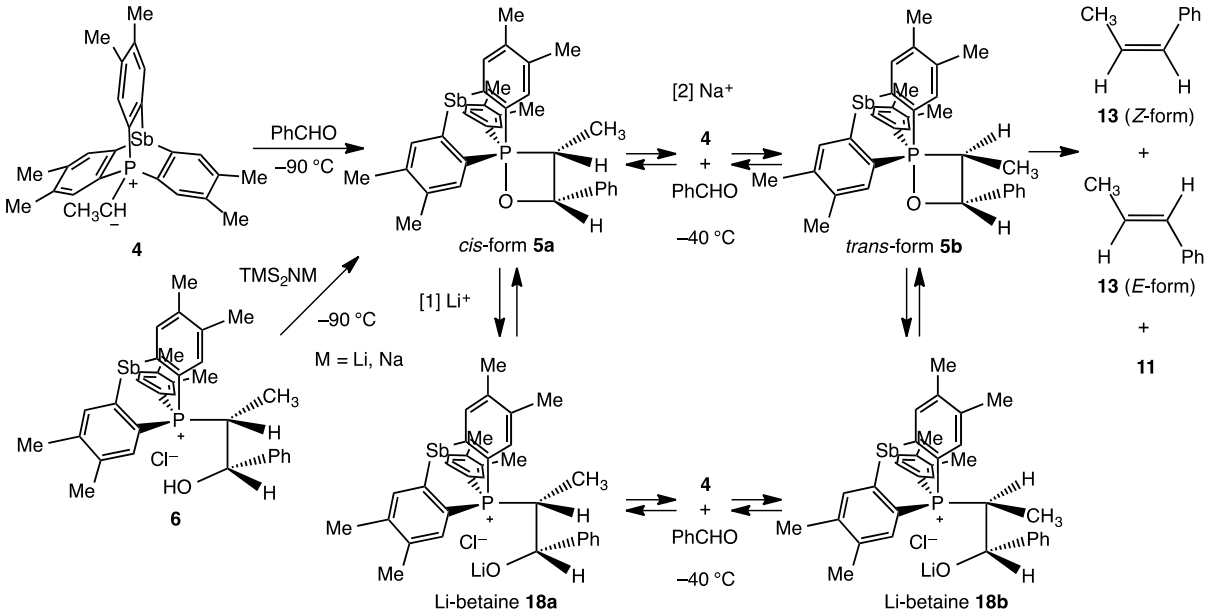
Table 4: 1,2-Oxaphosphentanes (phosphastibatriptycene and triphenyl systems)

	17a	**17b**	**9a**	**9b**
$G_{at\ 298\ K}$ (hartree)	-1463.653813	-1463.657380	-1460.070517	-1460.073292
ΔG^0 (kcal/mol)	0	–2.24	0	–1.74
Imaginary Freq.	0	0	0	0
P–C3	1.91643	1.92416	1.89927	1.91145
P–CAr(eq)	1.85635	1.85351	1.84167	1.85846
P–CAr(eq)	1.86177	1.87197	1.86076	1.86095
P–CAr(ap)	1.96949	1.96166	1.93411	1.93614
P–Oap	1.84172	1.82500	1.85253	1.85091
CAr(ap)–P–CAr(eq) (°)	93.40283	92.3393	94.02937	95.30836
CAr(ap)–P–CAr(eq) (°)	97.17347	99.01676	99.04173	98.32876
CAr(eq)–P–CAr(eq) (°)	109.48025	108.13262	112.28145	111.23419
CAr(ap)–P–O (°)	169.67412	166.16308	167.63121	166.10676
C3–P–CAr(ap) (°)	97.05138	96.39289	95.70265	93.55607
C3–P–CAr(eq) (°)	121.21984	114.57332	112.01232	122.11006

C3–P–CAr(eq) (°)	126.12996	134.26134	132.31516	123.76590
C3–P–O (°)	73.40465	73.50808	73.42137	73.14877
C4–C3–P (°)	89.37530	89.50300	88.45767	89.97159
C3–C4–O (°)	98.58898	98.82216	98.10098	98.68090
C4–O–P (°)	97.05064	97.75162	94.77404	96.61321
P–C_3–C_4–O (°)	10.30318	5.2512	18.83528	10.37712
P···M	3.50334	3.50847		
^{31}P NMR (ppm)	427.091	424.438	414.632	415.174
δ_P (from H_3PO_4)	-48.73	-46.07	-36.27	-36.81

B3LYP/6-31G(d) for C,H,P,O, lanl2dz for Sb, GIAO for NMR, δ_P 378.365 ppm (H_3PO_4)

Wittig reaction mechanism



Scheme 7

We have proposed a reaction mechanism for the (*E*)-selective Wittig reaction of non-stabilized phosphonium ylide **4** with benzaldehyde, as shown in Scheme 7, which was different from the Schlossor modification of the Wittig reaction.[43] The observation of two broad signals at –57.3 and –54.5 ppm for **5a** and **5b** at –80 °C and –40 °C in the reaction of **4** with benzaldehyde in the presence of lithium salt indicated that there are the equilibrium between *cis*-form **5a** and lithium complex of betaine **18a** at the temperature from –80 °C to –20 °C, and that between *trans*-form **5b** and lithium complex of betaine **18b** at those from –

40 °C to 0 °C as shown in the process [1] (Scheme 7). Isomerization from *cis*-form **5a** to *trans*-form **5b** was considered to occur at –40 °C *via* lithium complexes of betaines **18a** and **18b** and the equilibrium with the mixture of ylide **4** and benzaldehyde, resulting that (*E*)-alkene **13** was obtained as a major product (process [1]).

On the other hand, $^{31}P\{^{1}H\}$ NMR spectra in the reaction of **4** with benzaldehyde in the presence of sodium salt showed two sharp signals with the same half-width at –57.3 and –55.2 ppm at –80 °C and –40 °C, respectively, which were also observed by the deprotonation of *β*-hydroxyalkylphosphonium salt **6** with TMS_2NNa, indicating that there was no equilibration between 1,2-oxaphosphetane **5a** and betaine **18a** or that between **5b** with betaine **18b**. The isomerization from *cis*-form **5a** to *trans*-form **5b** clearly occurred at –40 °C as well as that in the presence of lithium salt. The crossover experiments for the deprotonation of **6** in the presence of *p*-chlorobenzaldehyde suggested that benzaldehyde was released from 1,2-oxaphosphetane **5a** at –40 °C as shown in process [2] (Scheme 7). The results indicated that *cis*-form **5a** in the phosphastibatriptycene system was selectively formed as the kinetic product at the initial step in the Wittig reaction like *cis*-form **9a** as major stereoisomer in the triphenylphosphine system. The (*E*)-selective Wittig reactions in the phosphastibatriptycene system in the presence of sodium salt were considered to proceeded under thermodynamic control *via* isomerization from *cis*-form **5a** to *trans*-form **5b**. The reversibility of the 1,2-oxaphosphetanes was observed in the presence of sodium salt even in the triphenylphosphine system as well as the previous report,[13] although the observed temperature was 0 °C, which was much higher than that (–40 °C) in the phosphastibatriptycene system. The aryl groups of the phosphastibatriptycene skeleton acted as electron-donating groups toward the cationic phosphorus center of non-stabilized phosphonium ylide **4** and a sterically hindered group toward the substituent at the 3-position of the 1,2-oxaphosphetane ring, while the phosphastibatriptycene skeleton did not affect the formation of *cis*-form **5a** in the initial kinetic process in the Wittig reaction. However, further investigations into the equilibria between 1,2-oxaphosphetanes and the starting materials at –40 °C are needed to reveal whether the mechanism involves a betaine or a [2+2] cycloadduct.

Conclusion

In this paper, the effect of a tridentate aryl ligand, a phosphastibatriptycene system, on the Wittig reaction was revealed for the first time in comparison with the results of the triphenylphosphine system. The Wittig reactions of non-stabilized phosphonium ylide **4** bearing a phosphastibatriptycene skeleton with benzaldehydes gave (*E*)-alkenes selectively in

the presence of both lithium and sodium salts, in contrast to the reactions of triphenylphosphonium ylide **7** with benzaldehydes, which gave *Z*-alkenes as the major products under the same conditions.

In the VT-$^{31}P\{^1H\}$ NMR spectra of the reaction of **4** with benzaldehyde in the presence of sodium salt, two intermediates were observed as sharp signals at –57.3 and –55.2 ppm at the different temperatures, –80 °C and –40 °C, respectively, which were assigned to *cis*- and *trans*-1,2-oxaphosphetanes **5a** and **5b** from the results of the deprotonation of *β*-hydroxyalkylphosphonium salt **6** with TMS_2NNa at the adapted temperature and the P–H and H–H coupling constants of methine protons at the 3- and 4-positions of the intermediates. The VT-$^{31}P\{^1H\}$ NMR spectra in the presence of sodium salt also showed that *cis*-1,2-oxaphosphetane **5a** isomerized to *trans*-form **5b** at –40 °C. The results clearly showed that *cis*-form **5a** was formed as the kinetic product in the initial step of the Wittig reaction and *trans*-form **5b** was produced as the thermodynamic product through the isomerization above –40 °C. On the other hand, only one intermediate, 1,2-oxaphosphetane **9**, was observed in the reaction of **7** with benzaldehyde during the VT-experiment as well as the previous report,[15] indicating that the two signals superposed or that the other signal was too small to be detected. Both crossover experiments in the reactions of *β*-hydroxyalkylphosphonium salts **6** and **10** with TMS_2NNa in the presence of *p*-chlorobenzaldehyde gave four corresponding alkenes. The observation of four 1,2-oxaphosphetanes **5** and **5'** at –40 °C and two 1,2-oxaphosphetanes **9** and **9'** at 0 °C during the VT-NMR measurements showed the existence of the equilibrium between 1,2-oxaphosphetanes and the starting materials. The results indicated that the stereochemical drift in the reactions of non-stabilized phosphonium ylide **4** with benzaldehydes occurred at much lower temperature than those of triphenylphosphonium ylide **7** and benzaldehydes even in the presence of sodium salt.

VT-NMR measurements in the presence of lithium salt showed broad signals for *cis*-form **5a** and *trans*-form **5b** and a broad signal for the corresponding Li-betaine at 19.2 ppm until –40 °C, which was different to the sharp peaks observed in the presence of sodium salt, while isomerization from **5a** to **5b** occurred at –40 °C. Crossover experiment using both lithium and sodium salts indicated that benzaldehyde was exchanged with *p*-chlorobenzaldehyde. The results indicated that isomerization from **5a** to **5b** occurred by equilibration between the 1,2-oxaphosphetane and the non-stabilized phosphonium ylide–benzaldehyde *via* a Li-betaine. However, it is still not clear whether the isomerization in the presence of sodium salt proceeds *via* a betaine intermediate or by [2+2]-cycloaddition.

Consequently, stereochemical drift resulted in highly (*E*)-selective alkenes being obtained from the Wittig reactions of **4** with benzaldehydes in the presence of both lithium and sodium salts. This occurred more easily than in the non-stabilized triphenylphosphonium ylide system and was similar to that of non-stabilized trialkylphosphonium ylides.[12,13] The phosphastibatriptycene skeleton, regarded as a tridentate ligand on the phosphorus atom, did not affect formation of the kinetic product in the initial step of the Wittig reactions of **4** and benzaldehydes, resulting in the highly selective generation of *cis*-form **5a** as well as that of triphenylphosphine system. In contrast, the phosphastibatriptycene skeleton strongly affected the isomerization of *cis*-form **5a** to more thermodynamically stable *trans*-form **5b** above –40 °C, which was a much lower temperature than that (0 °C) observed for the triphenylphosphine system. We are going to investigate the effects of bridgehead atom other than antimony on stereochemical drift.

Experimental section

General. ^{1}H, $^{13}C\{^{1}H\}$, and $^{31}P\{^{1}H\}$ NMR spectra were obtained by Bruker Advance-III 400 (400 MHz for ^{1}H, 100 MHz for ^{13}C, 162 MHz for ^{31}P) and Bruker Advance-II 600 (600 MHz for ^{1}H, 151 MHz for ^{13}C, and 243 MHz for ^{31}P) 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) and H_3PO_4 (δ_P 0.00). Melting points were measured by Yanaco MICRO MELTING POINT APPARATUS. ESI-MS was conducted by Exactive Plus of ThermoFisher Co. X-ray crystallographic analysis was performed by SMART APEX II of Bruker AXS Co. Gel permeation chromatography, GPC, using $CHCl_3$ as the eluent was performed by LC-908 of Japan Analytical Industry Co., Ltd. Reagents and solvents for synthesis were used in 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_2NLi and TMS_2NNa in THF made in KANTO were used for the generation of phosphonium ylides and deprotonation of β-hydroxyalkylphosphonium salts. Dried THF and Et_2O were used from the solvent cans of KANTO without any further purification. CH_2Cl_2 and $CHCl_3$ were distilled over CaH_2 to remove water from solvents. In the following data, TrpSbP denoted 2,3,6,7,14,15-hexamethyl-9-phospha-10-stibatriptycene.

Synthesis of tris(2-bromo-4,5-dimethylphenyl)phosphine 2[10]

Under nitrogen, to a THF (140 mL) and Et_2O (100 mL) solution of 4,5-dibromo-*o*-xylene (21.0 g, 80.0 mmol) in 500 mL three-necked round flask with thermometer and 100 mL

dropping funnel was added 1.58 M hexane solution of *n*-BuLi (50 mL, 80.0 mmol) from the funnel for 30 min with keeping the temperature below –100 °C, getting the pale yellow clear solution. An Et_2O (50 mL) solution of PCl_3 (1.70 mL, 26.6 mmol) was added to the reaction mixture at –110 °C for 10 min by a transfer silicon tube and the solution was stirred for 1 hour at the same temperature. The resulting solution was evaporated after the reaction mixture was allowed to warm to room temperature for 1 hour. The reaction mixture was treated with water (100 mL) and extracted with CH_2Cl_2 (200 mL x 2). The organic layer was washed with water (200 mL x 2) and aqueous NaCl (200 mL) and dried over $MgSO_4$. The organic solution was evaporated to give yellow oil, which was purified by a short length column chromatography (SiO_2) with $CHCl_3$ as an eluent to remove a polymeric material formed from the lithiation of dibromoxylene. The residue after evaporation was filtrated with hexane to give a white solid (3.93 g, 6.75 mmol) of pure triarylphosphine **2** in 25 % yield.

White solid (m.p. 225 ~ 230 °C, lit[10)] m.p. 249 ~ 250 °C)

^{1}H NMR ($CDCl_3$, 400 MHz) δ = 2.07 (s, 9H, CH_3), 2.25 (s, 9H, CH_3), 6.49 (d, $^4J_{PH}$ = 2.4 Hz, 3H), 7.40 (d, $^3J_{PH}$ = 4.0 Hz, 3H).

^{31}P NMR ($CDCl_3$, 162 MHz) δ = –4.76 (m).

Synthesis of 2,3,6,7,14,15-hexamethyl-9-phospha-10-stibatriptycene 1[10]

Under nitrogen, to a THF (100 mL) solution of triarylphosphine **2** (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 to **2**) from a 5 mL syringe at –90 °C to –85 °C for 5 min, to give deep yellow clear solution. The reaction mixture was stirred at –90 °C for 30 min. A THF (15 mL) solution of $SbCl_3$ (485 mg, 2.14 mmol) was added to the reaction mixture at –90 °C to –85 °C for 10 min by a transfer silicon tube from 50 mL two-neck round flask and the mixture was stirred for 1 h 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 x 3). The organic layer was washed with water (40 mL), 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 phosphastibatriptycene **1** as a white solid (111 mg, 0.237 mmol) in 14% yield. The purification method for **1** is not silica gel chromatography and GPC but just the filtration, which improved on the previous reported one[9].

White solid (m.p. 295 ~ 300 °C, lit[10] m.p. > 300 °C)

^{1}H NMR ($CDCl_3$, 600 MHz) δ = 2.18 (s, 9H, CH_3), 2.19 (s, 9H, CH_3), 7.69 (s, 3H), 7.90 (d, $^3J_{PH}$ = 12.0 Hz, 3H).

^{31}P{^{1}H} NMR ($CDCl_3$, 243 MHz) δ = –10.8 (s).

Synthesis of 9-ethyl-2,3,6,7,14,15-hexamethyl-9-phosphonio-10-stibatriptycene Iodide 3[28,29]

Under nitrogen, a $CHCl_3$ (5 mL) solution of phosphastibatriptycene **1** (57 mg, 0.123 mmol) and ethyl iodide (40 μL, 0.500 mmol) was heated at 70 °C for 11 days. $CHCl_3$ (2 mL) was added to the reaction mixture before the reaction solvent was completely evaporated under the heating condition. Further ethyl iodide (20 μL, 0.250 mmol) was added to the reaction mixture after 8 days. The reaction mixture was evaporated after the stirring for 11 days and the residue was filtrated with THF to give a pale yellow solid (64 mg, 0.103 mmol) of ethylphosphonium iodide **3** in 84 % yield.

Pale yellow solid, m.p. 237-241 °C

^{1}H NMR (600 MHz, $CDCl_3$) δ□□□□□□□□□□dt, $^3J_{PH}$ = 18.6 Hz, $^3J_{HH}$ = 7.2 Hz, □□□□H$_{Et}$□, 2.27 (s, 9H, H$_{Me}$), 2.36 (s, 9H, H$_{Me}$), 4.20 (dq, $^2J_{PH}$ = 13.2 Hz, $^3J_{HH}$ = 7.6 Hz, 2H, H$_{Et}$), 7.85 (d, $^4J_{PH}$ = 3.6 Hz, 3H, 4,5,16-H), 8.01 (d, $^3J_{PH}$ = 10.8 Hz, 3H, 1,8,13-H)

^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ□□□7.85 (p, $^2J_{PC}$ = 5.7 Hz, C$_{Et}$), 9.25 (s, $^1J_{PC}$ = 48.5 Hz, C$_{Et}$), 19.8 (p, C$_{Me}$), 19.9 (p, C$_{Me}$), 122.5 (q, $^1J_{PC}$ = 92.4 Hz), 132.4 (t, $^2J_{PC}$ = 13.3 Hz), 138.8 (t, $^3J_{PC}$ = 11.0 Hz), 139.4 (q, $^2J_{PC}$ = 12.2 Hz), 141.3 (q, $^4J_{PC}$ = 2.7 Hz), 142.8 (q, $^3J_{PC}$ = 10.1 Hz)

^{31}P{^{1}H} NMR (243 MHz, $CDCl_3$) δ□□□□12.2 (s)

ESI-MS (positive, CH_3CN) *m/z* 493.1053, calcd for $C_{26}H_{29}PSb$: 493.1040.

Synthesis of *erythro*-(1-hydroxy-1-phenyl-2-propyl)phosphonium chloride 6[29–31]

To a THF (10 mL) solution of ethylphosphonium iodide **3** (127 mg, 0.204 mmol) was added 1.63 M THF solution of TMS_2NNa (0.37 mL, 0.60 mmol) to generate non-stabilized phosphonium ylide **4** as a yellow clear solution at 0 °C and the reaction mixture was stirred for 10 min. To the THF solution cooled to –100 °C was added benzaldehyde (0.10 mL, 0.70 mmol). The resulting mixture was stirred for 5 min at –100 °C and bubbled gaseous HCl generated from NaCl–H_2SO_4 to give the pale yellow solution. The reaction mixture was allowed to warm to room temperature for 1 hour and the solution was evaporated to give the crude material, which was filtered with $CHCl_3$ for purification by GPC. *β*-Hydroxyalkylphosphonium salt **6** (77 mg, 0.11 mmol, 54%) was obtained as the pale

yellow solid after the evaporation of fraction NO.2 with 44 min of the retention time.
Pale yellow solid (m.p. 192 ~ 200 °C)
^{1}H NMR ($CDCl_3$, 600 MHz) δ = 1.97 (dd, $^{3}J_{PH}$ = 17.7 Hz, $^{3}J_{HH}$ = 7.5 Hz, 3H, CH_3), 2.27 (s, 9H, CH_3), 2.32 (s, 9H, CH_3), 4.97–5.03 (m, 2H, CH and OH), 6.50 (br d, $^{2}J_{PH}$ = 9.6 Hz, 1H, CH), 7.40 (t, $^{3}J_{HH}$ = 7.2 Hz, 1H, $H_{p\text{-Ph}}$), 7.51 (t, $^{3}J_{HH}$ = 7.2 Hz, 2H, $H_{m\text{-Ph}}$), 7.83-7.85 (m, 5H, $H_{o\text{-Ph}}$, 4,5,16-H), 8.24 (br, 3H, 1,8,13-H).
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ □□13.2 (p, α-CH_3), 19.7 (p, CH_3), 20.2 (p, CH_3), 32.9 (t, $^{2}J_{PC}$ = 41.4 Hz, β-CH), 70.3 (t, $^{1}J_{PC}$ = 3.8 Hz, α-CH), 127.0 (t, Ph), 127.5 (q, $C_{4a,10a,11}$), 128.2 (t, Ph), 129.1 (t, Ph), 134.1 (t, $C_{1,8,13}$), 138.7 (t, $^{3}J_{PC}$ = 11.0 Hz, $C_{4,5,16}$), 139.0 (q, $^{3}J_{PC}$ = 12.1 Hz, $C_{2,7,14}$), 140.9 (q, Ph), 142.9 (q, $C_{3,6,15}$). A quaternary signal for $C_{8a,9a,12}$ was not observed in ^{13}C NMR spectra, but HMBC was observed the correlation between 4,5,16-H at 7.83 ppm in ^{1}H NMR spectrum and $C_{8a,9a,12}$ at around 124 ppm in ^{13}C NMR spectrum.
^{31}P{1H} NMR ($CDCl_3$, 243 MHz) δ = 18.2 (s)
ESIMS (positive, CH_3CN) *m/z* 599.1463, calcd for $C_{33}H_{35}OPSb$: 599.1458.

Synthesis of Ethyltriphenylphosphonium iodide 8

Triphenylphosphine (2.62 g, 10.0 mmol) was reacted with ethyl iodide (4.40 g, 28.2 mmol) in CH_2Cl_2 (20 mL) at room temperature for 15 min to give ethyltriphenylphosphonium iodide (3.93 g, 9.40 mmol) as white solid in 95% yields, which was obtained after filtration with THF to remove ethyl iodide from the reaction mixture.
White solid (m.p. 164 ~ 165.5 °C, lit[28] m.p. 164 ~ 165 °C)
^{1}H NMR ($CDCl_3$, 600 MHz) δ = 1.40 (dt, $^{3}J_{PH}$ = 20.4 Hz, $^{3}J_{HH}$ = 7.2 Hz, 3H, CH_3), 3.79 (dq, $^{2}J_{PH}$ = 12.3 Hz, $^{3}J_{HH}$ = 7.2 Hz, 2H, CH_2), 7.70–7.73 (m, 6H, Ph-H), 7.80–7.85 (m, 9H, Ph-H).
^{31}P{^{1}H} NMR ($CDCl_3$, 243 MHz) δ = 26.3 (s).

Synthesis of *threo*- and *erythro*-(1-hydroxy-1-phenyl-2-propyl)triphenylphosphonium chlorides 10

To a THF (10 mL) solution of ethylphosphonium iodide **8** (208 mg, 0.498 mmol) was added 1.63 M THF solution of TMS_2NNa (0.48 mL, 0.78 mmol) at 0 °C to give a yellow clear solution of non-stabilized phosphonium ylide **7** and the reaction mixture was stirred for 10 min. To the THF solution cooled to –90 °C was added benzaldehyde (0.10 mL, 0.70 mmol). The resulting mixture was stirred for 10 min at –90 °C and gaseous HCl generated from NaCl–H_2SO_4 was bubbled to the reaction mixture to give the pale yellow solution. The reaction mixture was allowed to warm to room temperature for 1 hour and the solution was

evaporated to give the crude material, which was filtered with $CHCl_3$ for purification by GPC. *β*-Hydroxyalkylphosphonium salts **10** (196 mg, 0.453 mmol, 91%) were obtained as the pale yellow solid after the evaporation of fraction No.1 with 45 min of the retention time.

Pale yellow solid (m.p. 192 ~ 200 °C)

threo:*erythro* (10:90) ^{1}H NMR ($CDCl_3$, 600 MHz) δ = 1.27 (dd, $^3J_{PH}$ = 18.6 Hz, $^3J_{HH}$ = 7.2 Hz, 2.7H, CH_3), 1.37 (dd, $^3J_{PH}$ = 18.6 Hz, $^3J_{HH}$ = 7.2 Hz, 0.3H, CH_3), 3.88 (ddd, $^2J_{PH}$ = 18.6 Hz, $^3J_{HH}$ = 7.2, 2.4 Hz, 0.9H, CH), 4.31 (ddd, $^2J_{PH}$ = 18.6 Hz, $^3J_{HH}$ = 7.2, 3.0 Hz, 0.1H, CH), 4.54 (brs, 1H, OH), 5.44 (dd, $^3J_{HH}$ = 6.6, 2.4 Hz, 0.1H, CH), 5.46 (dd, $^3J_{HH}$ = 6.6, 3.0 Hz, 0.9H, CH), 7.24 (t, $^3J_{HH}$ = 7.2 Hz, 0.9H, $H_{p\text{-}Ph}$), 7.30 (t, $^3J_{HH}$ = 7.2 Hz, 0.1H, $H_{p\text{-}Ph}$), 7.31 (t, $^3J_{HH}$ = 7.2 Hz, 1.8H, $H_{m\text{-}Ph}$), 7.35 (t, $^3J_{HH}$ = 7.2 Hz, 0.2H, $H_{m\text{-}Ph}$), 7.46 (t, $^3J_{HH}$ = 7.2 Hz, 1.8H, $H_{o\text{-}Ph}$), 7.56 (t, $^3J_{HH}$ = 7.2 Hz, 0.2H, $H_{o\text{-}Ph}$), 7.70–7.76 (m, 6H, H_{Ph}), 7.78–7.83 (m, 3H, H_{Ph}), 7.85–7.93 (m, 6H, H_{Ph}).

threo:*erythro* (10:90) the *erythro* form was only observed: ^{13}C{^{1}H} NMR ($CDCl_3$, 151 MHz) δ □□10.2 (p, CH_3), 38.4 (t, $^2J_{PC}$ = 50.0 Hz, *β*-CH), 69.5 (t, $^1J_{PC}$ = 3.8 Hz, *α*-CH), 118.1 (q, $^1J_{PC}$ = 83.8 Hz), 126.3 (t, Ph), 127.9 (t, Ph), 128.5 (t, Ph), 130.3 (t, $^2J_{PC}$ = 23.4 Hz, Ph), 134.7 (t, $^2J_{PC}$ = 18.4 Hz, Ph), 134.8 (t, $^4J_{PC}$ = 3.0 Hz, Ph), 140.1 (t, $^3J_{PC}$ = 13.0 Hz, Ph).

^{31}P{^{1}H} NMR ($CDCl_3$, 243 MHz) δ = 30.7 (s), 30.9 (s).

ESI-MS (positive, CH_3CN) *m/z* 397.1711, calcd for $C_{27}H_{26}OP$; 397.1716.

2,3,6,7,14,15-Hexamethyl-9,10-phosphastibatriptycene *P*-oxide 11

The phosphine oxide bearing phosphastibatriptycene was obtained from the Wittig reaction of non-stabilized phosphonium ylide with benzaldehydes in the presence of lithium and sodium salts and purified by GPC to collect the fraction with 48 min of the retention time. The filtration of the crude material with hexane after evaporation provided the phosphine oxide **11** as pale yellow solid.

Pale yellow solid (m.p. 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, $^4J_{PH}$ = 4.2 Hz, 3H, 4,5,16-H), 8.09 (d, $^3J_{PH}$ = 10.8 Hz, 3H, 1,8,13-H).

^{31}P{^{1}H} NMR ($CDCl_3$, 243 MHz) δ = 22.7 (s).

^{13}C{^{1}H} NMR ($CDCl_3$, 151 MHz) δ □□19.45 (p, CH_3), 19.53 (p, CH_3), 131.9 (q, $^1J_{PC}$ = 108.0 Hz, $C_{8a,9a,12}$), 132.0 (t, $^2J_{PC}$ = 9.2 Hz, $C_{1,8,13}$), 137.4 (t, $^3J_{PC}$ = 11.5 Hz, $C_{4,5,16}$), 137.6 (q, $^3J_{PC}$ = 11.6 Hz, $C_{2,7,14}$), 138.3 (q, $^4J_{PC}$ = 2.4 Hz, $C_{3,6,15}$), 140.2 (q, $^2J_{PC}$ = 10.1 Hz, $C_{4a,10a,11}$).

APCI-MS (positive, CH_3CN) *m/z* 481.0684, calcd for $C_{24}H_{25}OPSb$; 481.0676.

The Wittig reactions using ethylphosphonium salts, bases (TMS_2NLi, TMS_2NNa), and benzaldehydes.

THF (0.5 mL) as a reaction solvent was placed in a NMR tube with a sealed capillary tube filled with acetone-d_6 as the lock solvent for NMR measurement. To a suspension of phosphonium salts in THF in the *J*-Young NMR tube was added TMS_2NM (M = Li or Na) at 0 °C to generate non-stabilized phosphonium ylides making the solution yellow. The phosphonium ylides reacted with benzaldehydes in THF (0.1 mL) at –90 °C. The mixture was allowed to warm to room temperature for 2.5 h. 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 ^1H NMR spectroscopy after the confirmation of no change of the spectra in the Wittig reaction for 12 h.

To estimate the products yields, ca. 21-25 mg of $Ph_2C{=}CH_2$ was dissolved in THF (1.00 mL) in a small sample tube and 0.10 mL of the THF solution measured by a 0.5 mL transfer pipette was added to a reaction NMR tube with *J*-young valve each reaction. The protons of signals of produced alkenes at around 4-6 ppm were compared with the singlet signal due to methylene protons of $Ph_2C{=}CH_2$.[44] The detail amounts of the starting materials, benzaldehydes, the products, and $Ph_2C{=}CH_2$ were described in each reaction.

The VT-^1H and $^{31}P\{^1H\}$ NMR spectra in the Wittig reaction were measured every 10 °C from –90 °C to 25 °C by accumulation on 128 of scan number after the addition of benzaldehydes in THF 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 NMR equipment.

The reaction of non-stabilized phosphonium ylide 4 or 7, which was generated from ethylphosphonium iodide 3 or 8 with TMS_2NM (M = Li or Na), with ArCHO gave (*E*):(*Z*)-alkenes 13-16 as follows.

(1) $TrpSbP{=}CHCH_3$ **4** + PhCHO: TMS_2NLi (62 μL, 80.6 μmol), $TrpSbP^+CH_2CH_3{\cdot}I^-$ **3** (10.5 mg, 17.0 μmol), PhCHO (2.50 μL, 2.60 mg, 24.5 μmol), $PhCH{=}CHCH_3$ **13** (1.16 mg, 9.81 μmol)/$Ph_2C{=}CH_2$ (2.14 mg, 11.9 μmol) = 0.825/1.00, Yield 58%, (*E*):(*Z*) = 97:3.

(2) $TrpSbP{=}CHCH_3$ **4** + *p*-ClC_6H_4CHO: TMS_2NLi (62 μL, 80.6 μmol), $TrpSbP^+CH_2CH_3{\cdot}I^-$ **3** (11.5 mg, 18.6 μmol), *p*-ClC_6H_4CHO (3.40 μL, 4.07 mg, 29.0 μmol), $ArCH{=}CHCH_3$ **14** (1.01 mg, 6.64 μmol)/$Ph_2C{=}CH_2$ (2.14 mg, 11.9 μmol) = 0.558/1.00, Yield 36%, (*E*):(*Z*) = 75:25.

(3) $TrpSbP{=}CHCH_3$ **4** + *p*-MeC_6H_4CHO: TMS_2NLi (62 μL, 80.6 μmol), $TrpSbP^+CH_2CH_3{\cdot}I^-$

3 (11.7 mg, 18.9 μmol), *p*-MeC_6H_4CHO (4.59 μL, 4.68 mg, 39.0 μmol), $ArCH{=}CHCH_3$ **15** (1.26 mg, 9.28 μmol)/$Ph_2C{=}CH_2$ (2.27 mg, 12.6 μmol) = 0.736/1.00, Yield 49%, (*E*):(*Z*) = 91:9.

(4) $TrpSbP{=}CHCH_3$ **4** + *p*-$MeOC_6H_4CHO$: TMS_2NLi (62 μL, 80.6 μmol), $TrpSbP^+CH_2CH_3{\cdot}I^-$ **3** (11.7 mg, 18.9 μmol), *p*-$MeOC_6H_4CHO$ (4.33 μL, 4.84 mg, 35.5 μmol), $ArCH{=}CHCH_3$ **16** (1.55 mg, 10.4 μmol)/$Ph_2C{=}CH_2$ (2.27 mg, 12.6 μmol) = 0.829/1.00, Yield 55%, (*E*):(*Z*) = 90:10.

(5) $Ph_3P{=}CHCH_3$ **7** + PhCHO: TMS_2NLi (62 μL, 80.6 μmol), $Ph_3P^+CH_2CH_3{\cdot}I^-$ **8** (10.7 mg, 25.6 μmol) + PhCHO (3.74 μL, 3.89 mg, 36.7 μmol), $PhCH{=}CHCH_3$ **13** (2.33 mg, 19.8 μmol)/$Ph_2C{=}CH_2$ (2.14 mg, 11.9 μmol) = 1.66/1.00, Yield 77%, (*E*):(*Z*) = 31:69.

(6) $Ph_3P{=}CHCH_3$ **7** + *p*-ClC_6H_4CHO: TMS_2NLi (62 μL, 80.6 μmol), $Ph_3P^+CH_2CH_3{\cdot}I^-$ **8** (10.6 mg, 25.4 μmol) + *p*-ClC_6H_4CHO (4.52 μL, 5.41 mg, 38.5 μmol), $ArCH{=}CHCH_3$ **14** (2.95 mg, 19.3 μmol)/$Ph_2C{=}CH_2$ (2.14 mg, 11.2 μmol) = 1.73/1.00, Yield 76%, (*E*):(*Z*) = 21:79.

(7) $Ph_3P{=}CHCH_3$ **7** + *p*-MeC_6H_4CHO: TMS_2NLi (62 μL, 80.6 μmol), $Ph_3P^+CH_2CH_3{\cdot}I^-$ **8** (11.7 mg, 28.0 μmol) + *p*-MeC_6H_4CHO (4.45 μL, 4.53 mg, 37.7 μmol), $ArCH{=}CHCH_3$ **15** (3.68 mg, 27.8 μmol)/$Ph_2C{=}CH_2$ (2.27 mg, 12.6 μmol) = 2.21/1.00, Yield 99%, (*E*):(*Z*) = 49:51.

(8) $Ph_3P{=}CHCH_3$ **7** + *p*-$MeOC_6H_4CHO$: TMS_2NLi (62 μL, 80.6 μmol), $Ph_3P^+CH_2CH_3{\cdot}I^-$ **8** (10.9 mg, 26.1 μmol) + *p*-$MeOC_6H_4CHO$ (4.32 μL, 4.83 mg, 35.5 μmol), $ArCH{=}CHCH_3$ **16** (3.55 mg, 23.9 μmol)/$Ph_2C{=}CH_2$ (2.27 mg, 12.6 μmol) = 1.90/1.00, Yield 91%, (*E*):(*Z*) = 72:28.

(9) $TrpSbP{=}CHCH_3$ **4** + PhCHO: TMS_2NNa (42 μL, 69.3 μmol), $TrpSbP^+CH_2CH_3{\cdot}I^-$ **3** (11.8 mg, 19.0 μmol) + PhCHO (3.42 μL, 3.63 mg, 34.2 μmol), $PhCH{=}CHCH_3$ **13** (1.95 mg, 16.5 μmol)/$Ph_2C{=}CH_2$ (1.70 mg, 9.44 μmol) = 1.75/1.00, Yield 87%, (*E*):(*Z*) = 87:13.

(10) $TrpSbP{=}CHCH_3$ **4** + *p*-ClC_6H_4CHO: TMS_2NNa (44 μL, 83.6 μmol), $TrpSbPCH_2CH_3{\cdot}I$ **3** (11.4 mg, 18.4 μmol) + *p*-ClC_6H_4CHO (3.75 μL, 4.48 mg, 31.9 μmol), $ArCH{=}CHCH_3$**14** (2.00 mg, 14.3 μmol)/$Ph_2C{=}CH_2$ (2.25 mg, 12.5 μmol) = 1.14/1.00, Yield 77%, (*E*):(*Z*) =

88:12.

(11) TrpSbP=CHCH$_3$ **4** + *p*-MeC$_6$H$_4$CHO: TMS$_2$NNa (62 μL, 80.6 μmol), TrpSbPCH$_2$CH$_3$·I **3** (11.4 mg, 18.4 μmol) + *p*-MeC$_6$H$_4$CHO (3.31 μL, 3.37 mg, 28.1 μmol), ArCH=CHCH$_3$ **15** (1.11 mg, 8.19 μmol)/Ph$_2$C=CH$_2$ (2.34 mg, 13.0 μmol) = 0.630/1.00, Yield 45%, (*E*):(*Z*) = 80:20.

(12) TrpSbP=CHCH$_3$+*p*-MeOC$_6$H$_4$CHO: TMS$_2$NNa (44 μL, 83.6 μmol), TrpSbPCH$_2$CH$_3$·I **3** (11.0 mg, 17.7 μmol) + *p*-MeOC$_6$H$_4$CHO (3.07 μL, 3.43 mg, 25.2 μmol), ArCH=CHCH$_3$ **16** (1.28 mg, 8.61 μmol)/Ph$_2$C=CH$_2$ (2.38 mg, 13.2 μmol) = 0.652/1.00, Yield 49%, (*E*):(*Z*) = 95:5.

(13) Ph$_3$P=CHCH$_3$ **7** + PhCHO: TMS$_2$NNa (48 μL, 79.2 μmol), Ph$_3$P$^+$CH$_2$CH$_3$·I$^-$ **8** (11.7 mg, 28.0 μmol) + PhCHO (3.52 μL, 3.73 mg, 35.2 μmol), PhCH=CHCH$_3$ **13** (2.86 mg, 24.2 μmol)/Ph$_2$C=CH$_2$ (1.70 mg, 9.44 μmol) = 2.56/1.00, Yield 87%, (*E*):(*Z*) = 22:78.

(14) Ph$_3$P=CHCH$_3$ **7** + *p*-ClC$_6$H$_4$CHO: TMS$_2$NNa (44 μL, 83.6 μmol), Ph$_3$P$^+$CH$_2$CH$_3$·I$^-$ **8** (12.0 mg, 28.7 μmol) + *p*-ClC$_6$H$_4$CHO (4.21 μL, 5.04 mg, 35.9 μmol), ArCH=CHCH$_3$ **14** (3.42 mg, 25.9 μmol)/Ph$_2$C=CH$_2$ (2.25 mg, 12.5 μmol) = 1.73/1.00, Yield 90%, (*E*):(*Z*) = 22:78.

(15) Ph$_3$P=CHCH$_3$ **7** + *p*-MeC$_6$H$_4$CHO: TMS$_2$NNa (44 μL, 83.6 μmol), Ph$_3$P$^+$CH$_2$CH$_3$·I$^-$ **8** (11.7 mg, 28.0 μmol) + *p*-MeC$_6$H$_4$CHO (3.89 μL, 3.97 mg, 33.0 μmol), ArCH=CHCH$_3$ **15** (2.76 mg, 20.9 μmol)/Ph$_2$C=CH$_2$ (2.57 mg, 14.3 μmol) = 1.46/1.00, Yield 75%, (*E*):(*Z*) = 25:75.

(16) Ph$_3$P=CHCH$_3$ **7** + *p*-MeOC$_6$H$_4$CHO: TMS$_2$NNa (44 μL, 83.6 μmol), Ph$_3$P$^+$CH$_2$CH$_3$·I$^-$ **8** (11.1 mg, 26.6 μmol) + *p*-MeOC$_6$H$_4$CHO (4.49 μL, 4.49 mg, 33.0 μmol), ArCH=CHCH$_3$ **16** (3.90 mg, 26.3 μmol)/Ph$_2$C=CH$_2$ (2.30 mg, 12.7 μmol) = 2.06/1.00, Yield 99%, (*E*):(*Z*) = 28:72.

Deprotonation of *β*-hydroxyalkylphosphonium salts with TMS$_2$NM (M = Li or Na).
THF (0.5 mL) as a reaction solvent was placed in a NMR tube with a sealed capillary tube filled with acetone-d_6 as the lock solvent for NMR measurement. To a solution of

β-hydroxyalkylphosphonium salt **6** or **10** in THF in the *J*-Young NMR tube was added TMS_2NM (Li or Na) at –90 °C. The mixture was allowed to warm to room temperature for 2.5 h. Yields were estimated by using a singlet signal due to the methylene protons of $Ph_2C{=}CH_2$ [44] in THF (0.1 mL) as an internal standard after the confirmation of no change of the spectra in deprotonations for 12 h. The signals at around 4-6 ppm of the protons of the produced alkenes were focused for the estimation of the yields.
The VT-^{1}H and $^{31}P\{^1H\}$ NMR spectra in deprotonation were measured every 10 °C from –90 °C to 25 °C by accumulation on 128 of scan number. The measurements at each target temperature were performed after ca. 5 min for getting the constant temperature by the thermo-monitor in NMR equipment.

(1) TrpSbPCHMeCHPhOH·Cl **6** + TMS_2NLi: TMS_2NLi (50 μL, 65 μmol), TrpSbPCHMeCHPhOH·Cl **6** (9.83 mg, 15.5 μmol), PhCH=CHMe **13** (0.77 mg, 6.55 μmol)/$Ph_2C{=}CH_2$ (3.32 mg, 18.4 μmol) = 0.356/1.00, Yields 42%, (*E*):(*Z*) = 70:30.

(2) TrpSbPCHMeCHPhOH·Cl **6** + TMS_2NLi + ArCHO: TMS_2NLi (50 μL, 65 μmol), TrpSbPCHMeCHPhOH·Cl **6** (7.55 mg, 10.3 μmol) + *p*-ClC_6H_4CHO (2.17 mg, 15.4 μmol), PhCH=CHMe **13** + ArCH=CHMe **14** (**13**:**14** = 37:63, **13**; 0.278 mg, 2.32 μmol, 23%, **14**; 0.596 mg, 3.86 μmol, 38%)/$Ph_2C{=}CH_2$ (2.35 mg, 13.1 μmol) = 0.472(0.375:0.625)/1.00, Yields 61%, Ph; (*E*):(*Z*) = 99:1, Ar; (*E*):(*Z*) = 99:1.

(3) TrpSbPCHMeCHPhOH·Cl **6** + TMS_2NNa: TMS_2NNa (44 μL, 83.6 μmol), TrpSbPCHMeCHPhOH·Cl **6** (10.1 mg, 16.9 μmol), PhCH=$CHCH_3$ **13** (1.26 mg, 10.7 μmol)/$Ph_2C{=}CH_2$ (2.25 mg, 12.5 μmol) = 0.855/1.00, Yield 63%, (*E*):(*Z*) = 15:85.

(4) TrpSbPCHMeCHPhOH·Cl **6** + TMS_2NNa at –40 °C for 1 hr: TMS_2NNa (44 μL, 83.6 μmol), TrpSbPCHMeCHPhOH·Cl **6** (12.5 mg, 17.2 μmol), PhCH=$CHCH_3$ **13** (0.563 mg, 4.76 μmol)/$Ph_2C{=}CH_2$ (2.52 mg, 14.0 μmol) = 0.34/1.00, Yield 28%, (*E*):(*Z*) = 69:31, PhCHO (0.0708 mg, 0.668 μmol)/$Ph_2C{=}CH_2$ (2.52 mg, 14.0 μmol) = 0.0477/1.00, Yield 4%.

(5) TrpSbPCHMeCHPhOH·Cl **6** + TMS_2NNa + ArCHO: TMS_2NNa (44 μL, 83.6 μmol), TrpSbPCHMeCHPhOH·Cl **6** (9.8 mg, 15.4 μmol) + *p*-ClC_6H_4CHO (3.79 μL, 4.53 mg, 32.2 μmol), PhCH=$CHCH_3$ **13** + ArCH=$CHCH_3$ **14** (**13**:**14** = 56:44, **13**; 0.320 mg, 2.71 μmol, 18%, **14**; 0.325 mg, 2.13 μmol, 14%)/$Ph_2C{=}CH_2$ (2.27 mg, 12.6 μmol) = 0.384(0.215:0.169)/1.00,

Yield 32%, **13**; (*E*):(*Z*) = 22:78, **14**; (*E*)/(*Z*) = 78:22.

(6) TrpSbPCHMeCHPhOH·Cl **6** + TMS_2NNa + ArCHO at –40 °C for 1 hr: TMS_2NNa (44 μL, 83.6 μmol), TrpSbPCHMeCHPhOH·Cl **6** (12.4 mg, 17.0 μmol) + *p*-ClC_6H_4CHO (3.79 μL, 4.53 mg, 32.2 μmol), PhCH=$CHCH_3$ **13** + ArCH=$CHCH_3$ **14** (**13**:**14** = 9:91, **13**; 0.152 mg, 1.29 μmol, 8%, **14**; 1.99 mg, 13.0 μmol, 76%)/$Ph_2C=CH_2$ (2.07 mg, 11.5 μmol) = 1.24(0.112:1.13)/1.00, Yield 84%, **13**; (*E*):(*Z*) = 0:100, **14**; (*E*):(*Z*) = 77:23.

(7) $Ph_3PCHMeCHPhOH·Cl$ **10** + TMS_2NNa: TMS_2NNa (44 μL, 83.6 μmol), $Ph_3PCHMeCHPhOH·Cl$ **10** (10.1 mg, 23.4 μmol), PhCH=$CHCH_3$ **13** (1.02 mg, 8.66 μmol)/$Ph_2C=CH_2$ (2.56 mg, 14.2 μmol) = 0.61/1.00, Yield 37%, (*E*):(*Z*) = 28:72, PhCHO (0.688 mg, 6.49 μmol)/$Ph_2C=CH_2$ (2.56 mg, 14.2 μmol) = 0.457/1.00, Yield 28%.

(8) $Ph_3PCHMeCHPhOH·Cl$ **10** + TMS_2NNa + PhCHO: TMS_2NNa (44 μL, 83.6 μmol), $Ph_3PCHMeCHPhOH·Cl$ **10** (10.9 mg, 25.2 μmol) + PhCHO (54.8 μL, 6.04 mg, 57.0 μmol), PhCH=$CHCH_3$ **13** (2.45 mg, 20.7 μmol)/$Ph_2C=CH_2$ (2.56 mg, 14.2 μmol) = 1.46/1.00, Yield 82%, (*E*):(*Z*) = 27:73.

(9) $Ph_3PCHMeCHPhOH·Cl$ **10** + TMS_2NNa + ArCHO: TMS_2NNa (44 μL, 83.6 μmol), $Ph_3PCHMeCHPhOH·Cl$ **10** (10.1 mg, 23.4 μmol) + *p*-ClC_6H_4CHO (4.88 μL, 5.84 mg, 41.5 μmol), PhCH=$CHCH_3$ **13** + ArCH=$CHCH_3$ **14** (**13**:**14** = 84:16, **13**; 1.44 mg, 12.2 μmol, 52%, **14**; 0.325 mg, 1.99 μmol, 9%)/$Ph_2C=CH_2$ (2.56 mg, 14.2 μmol) = 1.02(0.86:0.14)/1.00, Yield 61%, **13**; (*E*):(*Z*) = 26:74, **14**; (*E*):(*Z*) = 0:100.

(*E*):(*Z*)-alkenes 13-16

The protons of methyl and aryl groups of all alkenes were not detected in each spectrum due to overlap the signals of THF and other aryl groups.

(*E*)-1-phenyl-1-propene **13**

^{1}H NMR (600 MHz, THF-acetone-d_6)

δ = 5.52 (dq, $^3J_{HH}$ = 14.8, 6.6 Hz, 1H, 2-H), 5.67 (dq, $^3J_{HH}$ = 14.8, 1.7 Hz, 1H, 1-H).

(*Z*)-1-phenyl-1-propene **13**

^{1}H NMR (600 MHz, THF-acetone-d_6)

δ = 5.03 (dq, $^3J_{HH}$ = 11.5, 7.2 Hz, 1H, 2-H), 5.69 (dq, $^3J_{HH}$ = 11.5, 1.8 Hz, 1H, 1-H).

(*E*)-1-*p*-chlorophenyl-1-propene **14**

^{1}H NMR (600 MHz, THF-acetone-d_6)

δ = 5.56 (dq, $^3J_{HH}$ = 14.7, 6.5 Hz, 1H, 2-H), 5.66 (dq, $^3J_{HH}$ = 14.7, 1.8 Hz, 1H, 1-H).

(*Z*)-1-*p*-chlorophenyl-1-propene **14**

^{1}H NMR (600 MHz, THF-acetone-d_6)

δ = 5.08 (dq, $^3J_{HH}$ = 11.8, 7.3 Hz, 1H, 2-H), 5.69 (dq, $^3J_{HH}$ = 11.8, 1.8 Hz, 1H, 1-H).

(*E*)-1-*p*-methylphenyl-1-propene **15**

^{1}H NMR (600 MHz, THF-acetone-d_6)

δ = 5.45 (dq, $^3J_{HH}$ = 15.3, 6.6 Hz, 1H, 2-H), 5.62 (dq, $^3J_{HH}$ = 15.3, 1.3 Hz, 1H, 1-H).

(*Z*)-1-*p*-methylphenyl-1-propene **15**

^{1}H NMR (600 MHz, THF-acetone-d_6)

δ = 4.97 (dq, $^3J_{HH}$ = 11.8, 7.2 Hz, 1H, 2-H), 5.64 (dq, $^3J_{HH}$ = 11.7, 1.5 Hz, 1H, 1-H).

(*E*)-1-*p*-methoxyphenyl-1-propene **16**

^{1}H NMR (600 MHz, THF-acetone-d_6)

δ = 5.36 (dq, $^3J_{HH}$ = 15.6, 6.7 Hz, 1H, 2-H), 5.62 (dq, $^3J_{HH}$ = 15.7, 1.7 Hz, 1H, 1-H).

(*Z*)-1-*p*-methoxyphenyl-1-propene **16**

^{1}H NMR (600 MHz, THF-acetone-d_6)

δ = 4.97 (dq, $^3J_{HH}$ = 11.5, 7.1 Hz, 1H, 2-H), 5.64 (dq, $^3J_{HH}$ = 11.5, 1.7 Hz, 1H, 1-H).

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27) Phosphastibatriptycene **1** had previously been purified by GPC, but it has taken a few hours for the purification. In contrast, white solid was obtained by the filtration with the combination of AcOEt/hexane and acetone, which was much easier than the previous method.

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30) The TMSCl adduct of the betaine as the side product was obtained during the purification of *β*-hydroxyalkylphosphonium salt **6**. ^{1}H NMR (600 MHz, $CDCl_3$) δ = –0.41 (s, 9H, TMS), 1.73 (dd, $^{3}J_{PH}$ = 17.4 Hz, $^{3}J_{HH}$ = 7.8 Hz, 3H, CH_3), 2.20–2.41 (m, 18H, CH_3), 5.90–5.94 (m, 1H), 6.63 (dd, $^{3}J_{HH}$ = 4.8, 1.8 Hz, 1H), 7.42 (t, $^{3}J_{HH}$ = 7.2 Hz, 1H, *p*-Ph-H), 7.55 (t, $^{3}J_{HH}$ = 7.8 Hz, 2H, *m*-Ph-H), 7.77 (br s, 1H), 7.82 (br s, 1H), 7.92 (br s, 1H), 8.02 (d, $^{3}J_{HH}$ = 7.8 Hz, 2H, *o*-Ph-H), 8.06 (br d, J_{HH} = 0.5 Hz, 1H), 8.54 (br d, J_{HH} = 0.7 Hz, 1H), 8.66 (br d, J_{HH} = 0.7 Hz, 1H). ^{31}P{^{1}H} NMR (243 MHz, $CDCl_3$) δ = 17.42 (s). ESI-MS (CH_3CN) *m/z* 671.1862, calcd for $C_{36}H_{43}OPSbSi$: 671.1853.

31) The obtained *β*-hydroxyalkylphosphonium salt **6** by GPC contained 14 % amount of ethylphosphonium salt **3**, which was considered to be not iodide but chloride. ^{1}H NMR (600 MHz, $CDCl_3$) δ = 2.14 (dt, $^{3}J_{PH}$ = 18.6 Hz, $^{3}J_{HH}$ = 7.8 Hz, 3H, CH_3), 2.28 (s, 9H, CH_3), 2.36 (s, 9H, CH_3), 4.20 (m, 2H, CH_2), 7.82 (d, $^{4}J_{PH}$ = 3.6 Hz, 3H), 8.07 (d, $^{3}J_{PH}$ = 10.8 Hz, 3H). ^{31}P{^{1}H} NMR (243 MHz, $CDCl_3$) δ = 11.42 (s).

32) (a) Crystal data of **1**; Molecular Formula: $C_{24}H_{24}PSb$, Molecular Weight: 465.15, Crystal System: *rhombohedral*, Space Group: *R*-3, *Z*: 18, *a*: 20.086(1) Å, *b*: 20.086(1) Å, *c*: 26.775(1) Å, *α*: 90°, *β*: 90°, *γ*: 120°, *V*: 9355.5(5)Å^3, D_{calcd}: 1.486 gcm^{-3}, *F*(000): 4212, Temp: 103 K, No. of reflections measured Total/Unique: 17749/4886, No. of refinement variables: 242, *R*1(all data): 0.0583, *wR*2(all data): 0.1342, *GOF*: 1.089. Single crystals were obtained by recrystallization from chloroform. CCDC: 725597.[10] (b) Crystal data of **3**: Molecular Formula: $C_{26}H_{28}IPSb\cdot C_6H_5Cl$, Molecular Weight: 732.6, Crystal System: *orthorhombic*, Space Group: *P*bca, *Z*: 8, *a*: 12.0485(10) Å, *b*: 18.1149(15) Å, *c*: 27.520(2) Å, *α*: 90°, *β*: 90°, *γ*: 90°, *V*: 6006.3(9) Å^3, D_{calcd}: 1.620 gcm^{-3}, *F*(000): 2888, Temp: 120 K, No. of reflections measured Total/Unique: 33097/7134, No. of refinement variables: 332, *R*1(all data): 0.0331, *wR*2(all data): 0.0709, *GOF*: 1.027. Single crystals were obtained by recrystallization from chlorobenzene. CCDC: 1019729.[28]

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34) We have previously reported on the Wittig reaction of the non-stabilized and semi-stabilized phosphonium ylides bearing phosphastibatriptycene skeleton generated by *n*-BuLi with carbonyl compounds.[28] Four signals were observed as the intermediates in $^{31}P\{^{1}H\}$ NMR spectra, which were suggested to *trans*- and *cis*-1,2-oxaphosphetane together with each stereoisomer, *O*-apical and *C*-apical forms. However, two of four signals were due to the cleavage of Sb–C bonds of the intermediates by the attack of *n*-BuLi to antimony atom of the phosphastibatriptycene skeleton. Other two signals were in agreement with those of *trans*- and *cis*-1,2-oxaphospheatnes reporting in this paper. Therefore, the observed four signals were attributed to be not *O*-apical and *C*-apical forms of *trans*- and *cis*-1,2-oxaphosphetanes but the decomposed compounds.

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