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SOME REACTIONS OF *O*-EQUATORIAL SPIROPHOSPHORANES BEARING THE BIDENTATE LIGAND BASED ON DECAFLUORO-3-PHENYL-3-PENTANOL

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Abstract – Some reactions of *O*-equatorial and *O*-apical methylphosphoranes bearing two bidentate ligands consisted of 1,1,1,2,2,4,4,5,5,5-decafluoro-3-phenyl-3-pentanol were examined. Not only the *O*-apical phosphorane, but also the *O*-equatorial isomer did not react with MeLi as a nucleophile at the phosphorus center. This should be due to the steric bulkiness of the C_2F_5 group. For both isomers, deprotonation at the methyl group was achieved using Superbase (*t*-BuOK/*n*-BuLi) to give the corresponding α-anion, which was treated with several electrophiles to afford new phosphorane derivatives. The *O*-equatorial and *O*-apical phosphoranes having a *β*-hydroxyethyl group as the monodentate ligand were synthesized. It was found that under basic conditions, the *O*-apical phosphorane could be converted into the *O*-equatorial isomer via hexacoordinate phosphate intermediates.

INTRODUCTION

Hypervalent phosphorus compounds have attracted great interest because such species are assumed to be involved as intermediates (or transition states) in the biological phosphoryl transfer reaction.[1] Our group succeeded in isolating an isomeric pair of 10-P-5[2] phosphoranes (*O*-equatorial and *O*-apical) for the first time.[3] During the course of our study on the reactivity of both isomers, we reported that the *O*-equatorial spirophosphorane bearing the Martin ligands **1** showed an enhanced reactivity toward nucleophiles

compared to its stable isomer **2** (*O*-apical) (Figure 1).[4] For example, the reaction of **1** with MeLi afforded the monocyclic phosphorane **3**, while **2** did not react with MeLi under similar conditions (Scheme 1). This finding could be interpreted by the presence of a lower-lying $\sigma^*_{P\text{-}O}$ orbital as the reacting orbital in the equatorial plane, whereas the corresponding orbital is a higher-lying $\sigma^*_{P\text{-}C}$ orbital in the *O*-apical isomer. This was supported by the theoretical calculations, in which the energy level of the $\sigma^*_{P\text{-}O}$ orbital of **1a** was calculated to be lower than that of the $\sigma^*_{P\text{-}C}$ orbital of the *O*-apical isomer **2a** by 18.7 kcal mol^{-1}.[4] Moreover, the *O*-equatorial benzylic anion α to the phosphorus atom **4** was revealed to be more stable than the corresponding *O*-apical anion **5**.[4] This finding could also be explained by the existence of a strong $n_C \rightarrow \sigma^*_{P\text{-}O}$ interaction in the *O*-equatorial α-anion **4** (Scheme 2).

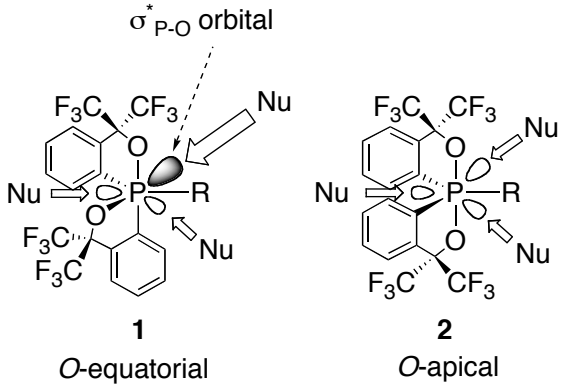
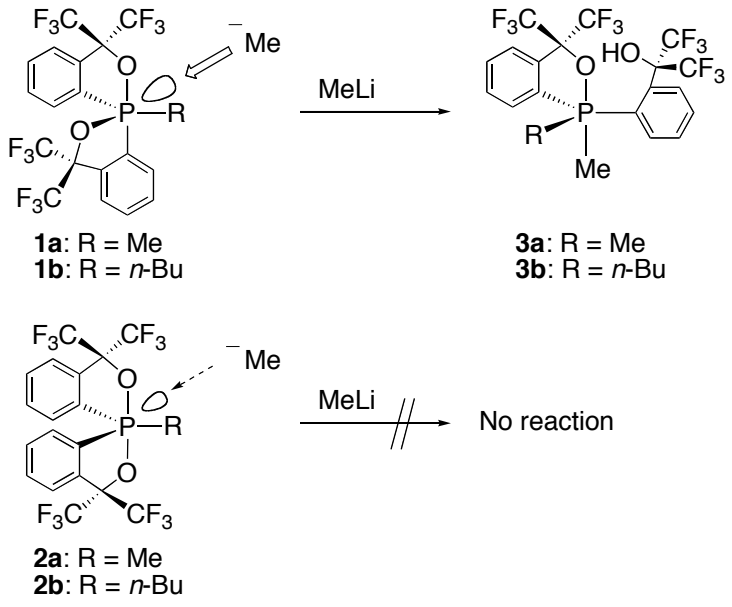
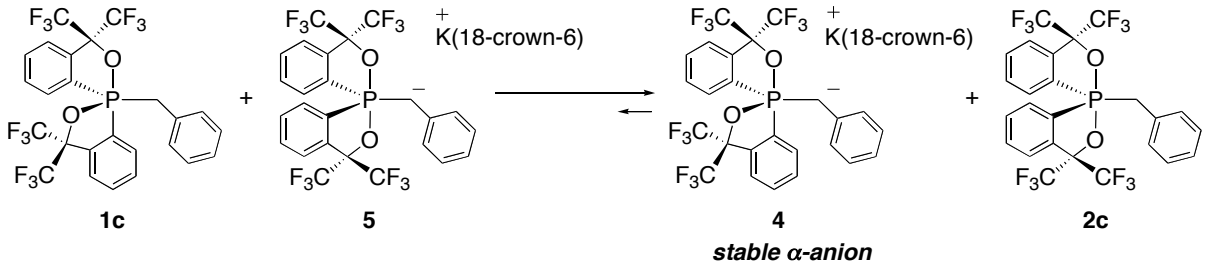


Figure 1

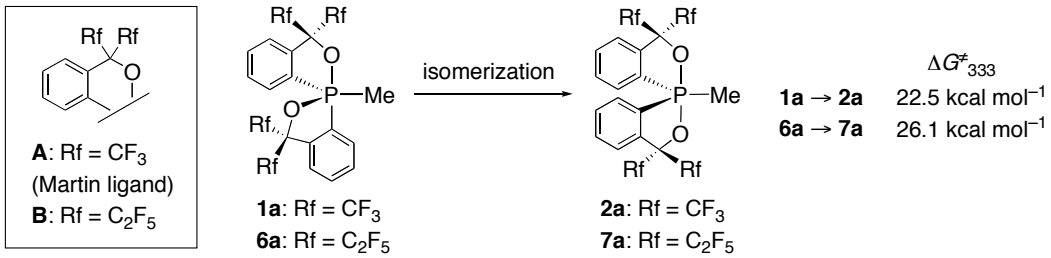


Scheme 1



Scheme 2

Very recently, we developed a new bidentate ligand based on decafluoro-3-phenyl-3-pentanol (**B**), and synthesized a family of pentacoordinate phosphoranes using this ligand. The kinetic study of the isomerization (**6a** to **7a**) unambiguously showed that the steric bulkiness of the C_2F_5 group was effective for freezing the pseudorotation (Scheme 3).[5] Moreover, the bidentate ligand was also found to be effective for freezing the pseudorotations of pentacoordinate organoarsenic compounds, providing the first isolation of the anti-apicophilic 10-As-5 species.[6] Therefore, it was of interest to investigate the steric effect on the reactivity of the newly prepared phosphoranes (**6** and **7**). We now discuss the reactivity of two isomeric phosphoranes bearing the C_2F_5 groups mainly focusing on the generation and reactions of the carbanion α to the phosphorus atom.



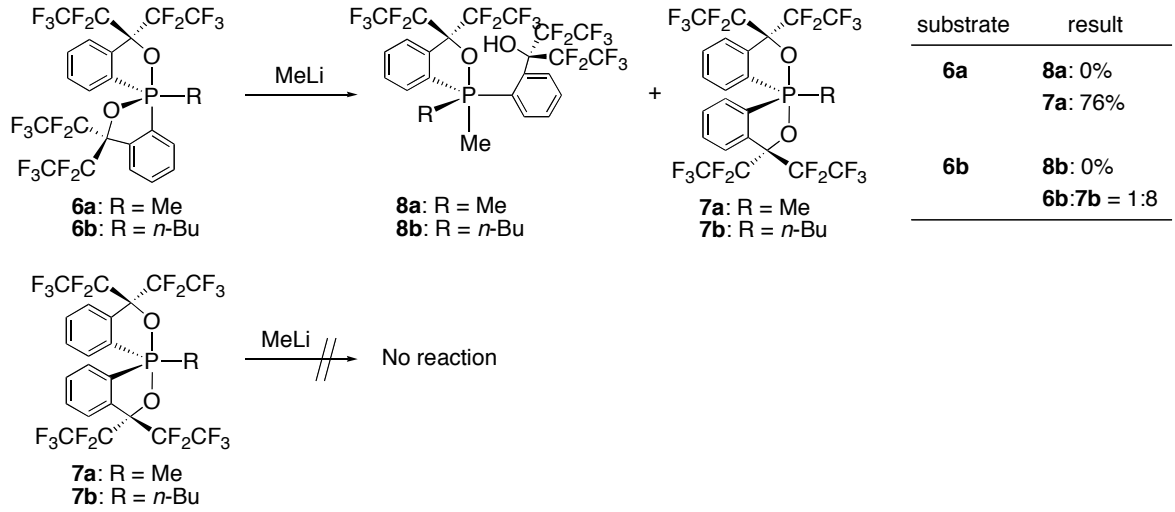
Scheme 3

RESULTS AND DISCUSSION

Reaction with a nucleophile

We first briefly examined the reactivity of the *O*-equatorial phosphoranes (**6a** and **6b**) toward a nucleophile. When the *O*-equatorial **6a** was treated with 3 equiv. of MeLi for 3 h at room temperature, the phosphorane **7a**, which is the more stable isomer of **6a**, was obtained in 76% yield (Scheme 4). In this reaction, the monocyclic phosphorane **8a** could not be observed. Similarly, in the case of the *n*-butyl derivative (**6b**), the *O*-apical isomer **7b** was mainly obtained (**6b** : **7b** = 1 : 8). On the other hand, for the *O*-apical phosphoranes (**7a** and **7b**), no reactions were observed under similar conditions as expected.

The nucleophilic reactions at the pentacoordinate phosphoranes are generally considered to take place within the equatorial plane, i.e., the nucleophile attacks a σ* orbital of one of the three equatorial bonds from the rear side.[4] For the Martin ligand system, our group proved this assumption, i.e., the *O*-equatorial **1b** reacted with MeLi to give the monocyclic phosphorane **3b** accompanying the breaking of one of the P—O bonds (Scheme 1).[4] However, the experimental result that **6** does not react with MeLi implies that the steric bulk of the pentafluoroethyl group could prevent the nucleophile (i.e., MeLi) from attacking the $\sigma^*_{P\text{-}O}$ orbital. The relatively rapid isomerization of **6** to **7** could be catalyzed by the lithium cation. Figure 2 shows the space filling models for the crystal structures of two *O*-equatorial *n*-butylphosphoranes **1b**[3] and **6b**. It is clear that the reaction space toward the $\sigma^*_{P\text{-}O}$ orbital of **6b** is narrower than that of **1b**. Though the apical P—O bond of **6b** (1.802(2) Å) is slightly (0.03 Å) longer than that of **1b** (1.768(3) Å), this small difference should not affect the crowding around the $\sigma^*_{P\text{-}O}$ orbital.



Scheme 4

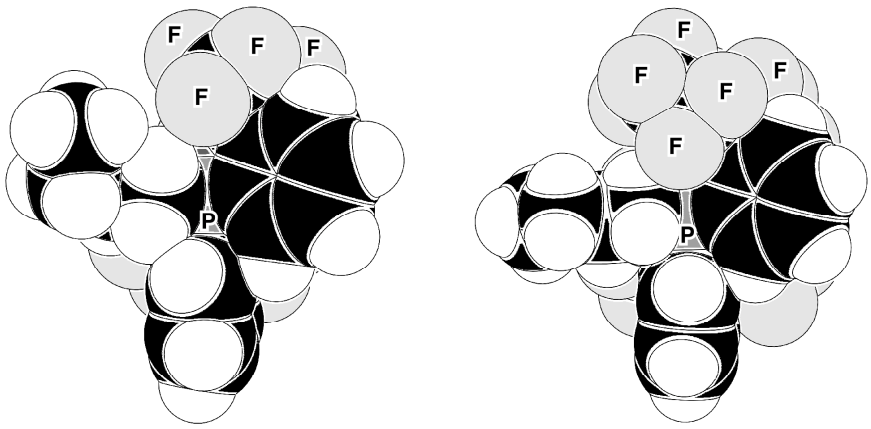
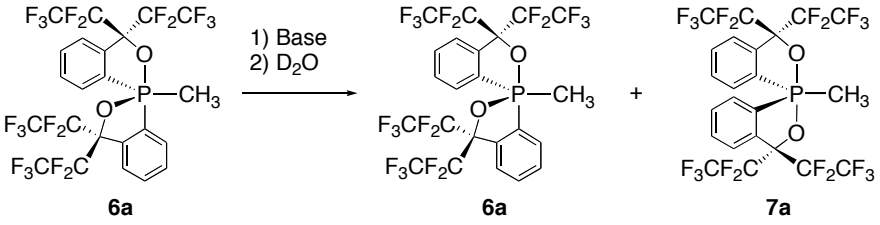


Figure 2. Space-filling representation of the crystal structure of *n*-butylphosphoranes (left: **1b**,[3] right: **6b**) viewed along the equatorial P—O bond.

Generation of an α-carbanion from *O*-equatorial methylphosphorane 6a

The result that no reaction between the $\sigma^*_{P\text{-}O}$ orbital of **6a** and MeLi was observed gave us a chance to generate an α-carbanion adjacent to the phosphorus atom without suffering from any nucleophilic side reactions. Therefore, we next examined the deprotonation at the methyl group of **6a** (Scheme 5 and Table 1). Using conventional strong bases (*n*-BuLi, *t*-BuLi, LDA, and NaHMDS), after quenching the reaction with D_2O, the starting material **6a** was recovered without being deuterated along with undeuterated *O*-apical phosphorane **7a** (Table 1). The ratio of **7a** ranged from 50 to 11% based on the ^{1}H NMR results. Apparently, such bases do not have the ability to deprotonate **6a**. Instead, they accelerated the stereomutation of **6a** to **7a**. It may imply that the lithium or sodium cation interacts with the oxygen atoms of **6a** to elongate the P—O bonds, and this might accelerate the isomerization of **6a** to **7a**.



Scheme 5

Table 1. Attempted deprotonation of **6a** using convensional strong bases.

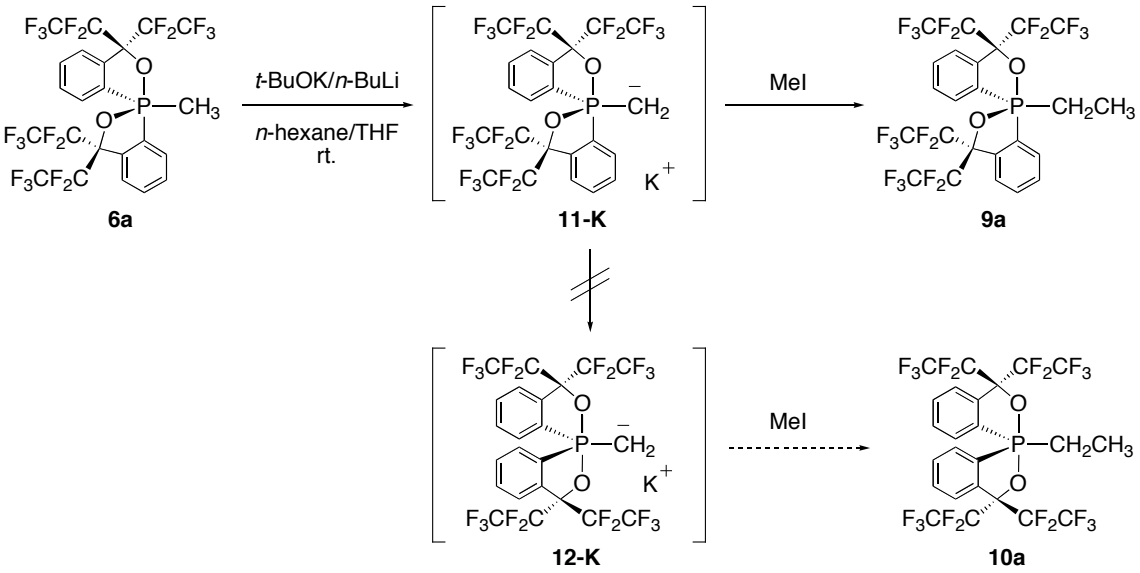
entry	base	solvent	condition	result[a]
1	*t*-BuLi (1.2 eq.)	Et_2O	rt, 0.25 h	**6a** : **7a** = 50 : 50
2	*n*-BuLi (1.2 eq.)	THF	0 °C, 0.5 h	**6a** : **7a** = 73 : 27
3	LDA (1.2 eq.)	THF	rt, 0.5 h	**6a** : **7a** = 87 : 13
4	NaHMDS (1.2 eq.)	THF	rt, 0.5 h	**6a** : **7a** = 89 : 11

a: Product ratio was calculated on the basis of the integral values in ^{1}H NMR.

Next, we chose the much stronger base, "Superbase",[7] which is a mixture of *t*-BuOK and *n*-BuLi (Scheme 6). When **6a** was treated with 1.5 equiv. of the Superbase prepared using *solid t*-BuOK, followed by the addition of MeI, **6a** was completely recovered (entry 1 in Table 2).[8] On the other hand, using 2 equiv. of the Superbase prepared using a THF solution of *t*-BuOK, a mixture of **9a** and **6a** (**9a** : **6a** = 83 : 17 based on ^{31}P NMR) was obtained (entry 2). These results obviously show that THF as the co-solvent is crucial for the deprotonation of **6a**, indicating that activation of the Superbase is needed.

The quantity of Superbase and the reaction time were examined in order to optimize the yield of **9a**. We found that 2 equiv. of Superbase and a 1 h reaction time were suitable for the generation of the

α-carbanion (entry 2). In these experiments, the starting material **6a** was recovered in all the experiments, and a longer reaction time provided a greater amount of **6a**. This should result from the proton abstraction of the α-carbanion from THF as the co-solvent. During these examinations, the *O*-apical isomers (**7a** or **10a**) were not observed at all (Scheme 6). This implies that the *O*-equatorial α-carbanion (**11-K**) is stabilized due to strong $n_C \rightarrow \sigma^*_{P\text{-}O}$ interaction, therefore, **11-K** does not isomerize into the corresponding *O*-apical isomer (**12-K**) at room temperature.



Scheme 6

Table 2. Examination of α-carbanion (**11-K**) generation using Superbase in *n*-hexane.

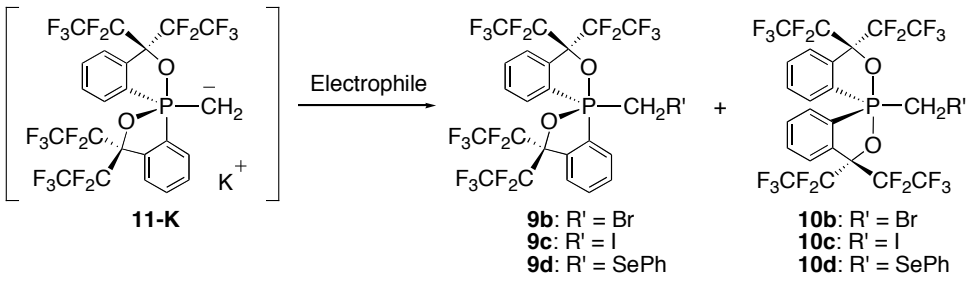
entry	Superbase[a] (eq.)	THF[d] (%)	time (h)[e]	result[f]
1	1.5[b]	0.0	1	**6a** : **9a** = 100 : 0
2	2[c]	3.0	1	**6a** : **9a** = 17 : 83
3	2[c]	3.0	3	**6a** : **9a** = 30 : 70
4	2[c]	3.0	5	**6a** : **9a** = 48 : 52
5	3[c]	4.5	1	**6a** : **9a** = 26 : 74
6	3[c]	4.5	3	**6a** : **9a** = 51 : 49

a: A 1 : 1 mixture of *t*-BuOK and *n*-BuLi. *b*: Solid *t*-BuOK was used. *c*: A THF (1 M) solution of *t*-BuOK was used. *d*: Content of the co-solvent THF. *e*: Reaction time for the deprotonation. *f*: Product ratio was calculated on the basis of the integral values in ^{1}H NMR.

Reactions of α-anion 11-K with electrophiles

The α-anion (**11-K**) reacted with several electrophiles to afford new phosphoranes (Scheme 7, Table 3).

When the α-anion **11-K** was treated with $BrCF_2CF_2Br$, the *O*-apical bromomethylphosphorane **10b** was obtained in 50% yield, however, the corresponding *O*-equatorial isomer (**9b**) was not observed (entry 1 in Table 3). As already described, the *O*-equatorial α-anion **11-K** does not isomerize into the corresponding *O*-apical isomer (**12-K**) even after 6 h at room temperature. Thus, the *O*-equatorial **9b** would be generated just after the addition of $BrCF_2CF_2Br$ and rapidly isomerizes into the *O*-apical **10b**. Using ICH_2CH_2I or PhSeBr as an electrophile, both the *O*-equatorial and *O*-apical phosphoranes were obtained. For the iodomethyl derivative, the *O*-equatorial **9c** gradually isomerized to the *O*-apical isomer **10c** at room temperature in solution, indicating that the assumption for the bromomethyl derivative should be valid. The yield of **9c** was found to be highly dependent on the temperature. Therefore, the reaction and the workup including extraction, washing and evaporation, were carried out at 0 °C, and the purification time using HPLC needed to be as short as possible for preventing the isomerization. On the other hand, the *O*-equatorial phenylselenomethyl derivative (**9d**) is stable in solution at room temperature.

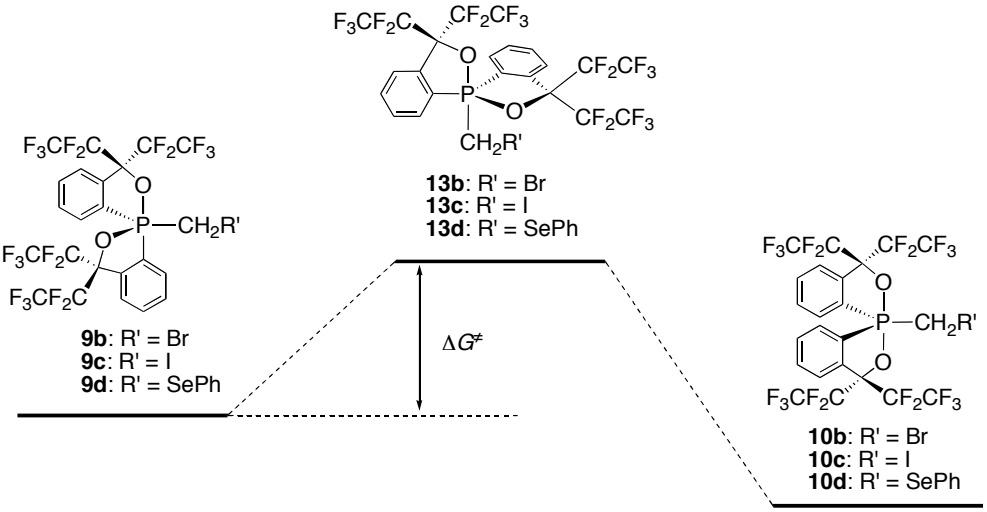


Scheme 7

Table 3. Reaction of α-anion **11-K** with electrophiles.

entry	electrophile	temp., time	R'	yield
1	$BrCF_2CF_2Br$	0 °C, 1 h	Br	**9b**: 0%, **10b**: 50%
2	ICH_2CH_2I	0 °C, 2 h	I	**9c**: 52%, **10c**: 5%
3	PhSeBr	r.t., 2.5 h	SePh	**9d**: 18%, **10d**: 14%

Qualitatively, the isomerization rates (**6a** to **7a**[5] < **9d** to **10d** < **9c** to **10c** < **9b** to **10b**) depend on the order of the electronegativity of substituent R' {Pauling's electronegativity scale: H (2.20) < Se (2.55) < I (2.66) < Br (2.96)}.[9,10] As previously proposed by our group,[11] during the stereomutation from **9** to **10**, the highest energy isomer bearing a more electronegative substituent at the apical site (**13**) becomes more stable; therefore, this reduces the activation free energy ($\Delta G^{\neq}$) of the stereomutation of **9** to **10** (Scheme 8). It should be noted that such *O*-equatorial compounds with an electronegative substituted methyl group were isolated for the first time in the C_2F_5 series, whereas in the CF_3 system, even the *O*-equatorial methylphosphorane (**1a**) was not stable to isomerization.[12]



Scheme 8

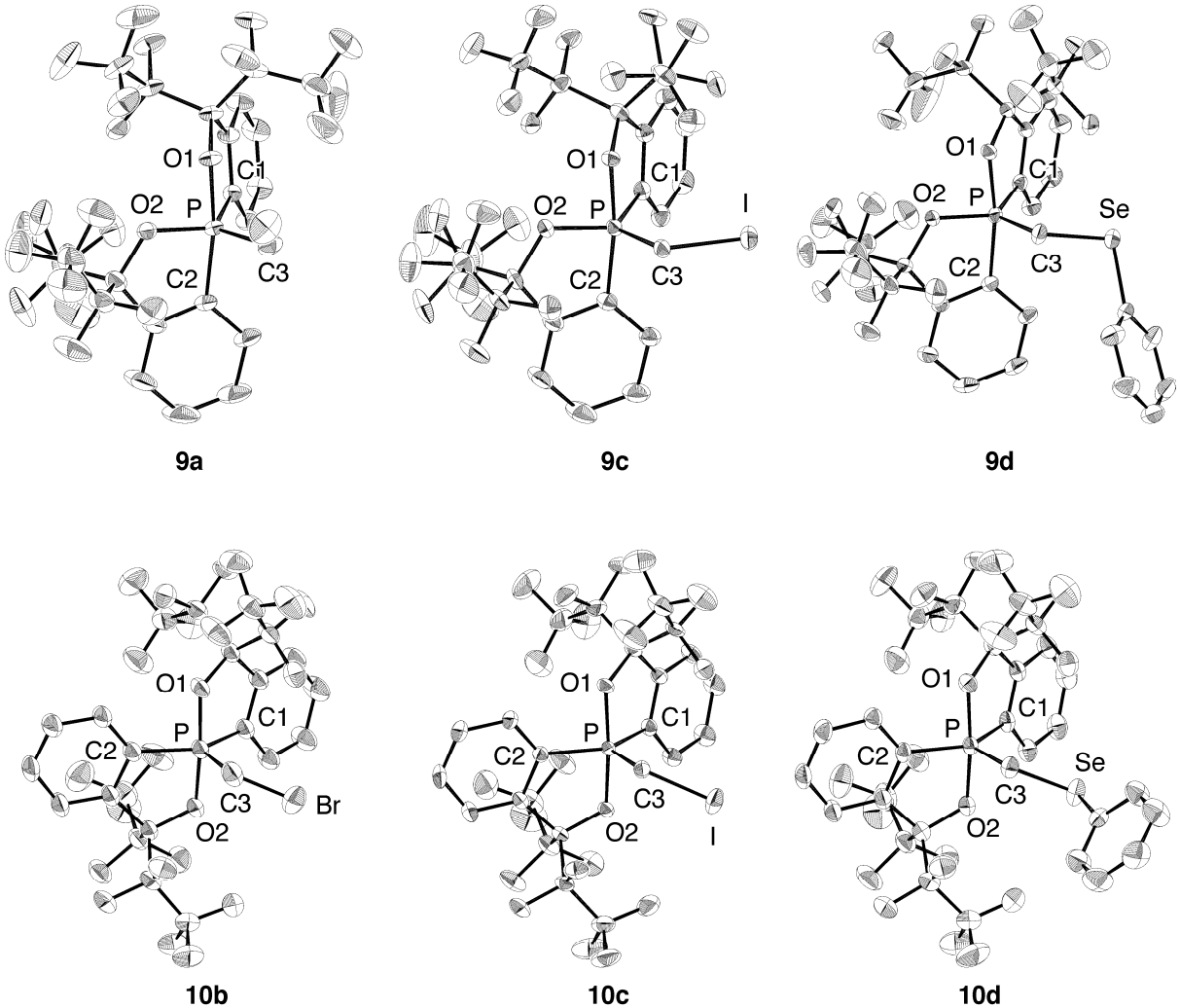


Figure 3. The ORTEP drawings of phosphoranes (**9a**, **9c**, **9d**, **10b**, **10c** and **10d**) showing the thermal ellipsoids at the 30% probability level. The hydrogen atoms are omitted for clarity.

Table 4. Selected bond lengths (Å) and angles (deg) for the phosphoranes.

Compound	**9a**	**9c**	**9d**	**10b**	**10c**	**10d**
Bond lengths (Å)						
P1—O1	1.7775(17)	1.787(4)	1.772(3)	1.746(4)	1.747(3)	1.745(4)
P1—O2	1.6585(19)	1.657(4)	1.655(3)	1.746(4)	1.748(3)	1.754(4)
P1—C1	1.828(2)	1.870(6)	1.825(4)	1.829(5)	1.829(4)	1.830(5)
P1—C2	1.874(3)	1.830(5)	1.886(4)	1.829(5)	1.824(3)	1.830(5)
P1—C3	1.839(3)	1.836(5)	1.845(4)	1.855(11)	1.823(4)	1.815(5)
Bond angles (deg)						
O1—P1—O2	83.57(9)	82.96(18)	82.77(13)	171.70(4)	171.89(13)	171.15(18)
O1—P1—C1	86.23(9)	86.30(2)	86.47(15)	87.40(2)	87.10(14)	87.20(2)
O1—P1—C2	170.72(11)	171.00(2)	170.56(15)	89.70(2)	89.94(15)	90.10(2)
O1—P1—C3	89.37(11)	87.70(2)	89.84(18)	94.12(15)	94.30(15)	94.40(2)
O2—P1—C1	119.54(10)	121.40(2)	122.52(16)	89.50(3)	89.49(15)	89.40(2)
O2—P1—C2	87.27(11)	88.30(2)	87.79(15)	87.40(2)	87.43(15)	86.60(2)
O2—P1—C3	120.40(14)	116.70(2)	115.37(17)	94.12(15)	93.77(16)	94.50(2)
C1—P1—C2	99.63(11)	100.50(3)	98.91(17)	139.10(4)	136.24(16)	135.30(2)
C1—P1—C3	118.87(14)	120.10(2)	120.89(18)	110.50(2)	109.15(16)	112.00(2)
C2—P1—C3	94.01(13)	94.00(3)	93.97(19)	110.50(2)	114.62(16)	112.60(2)

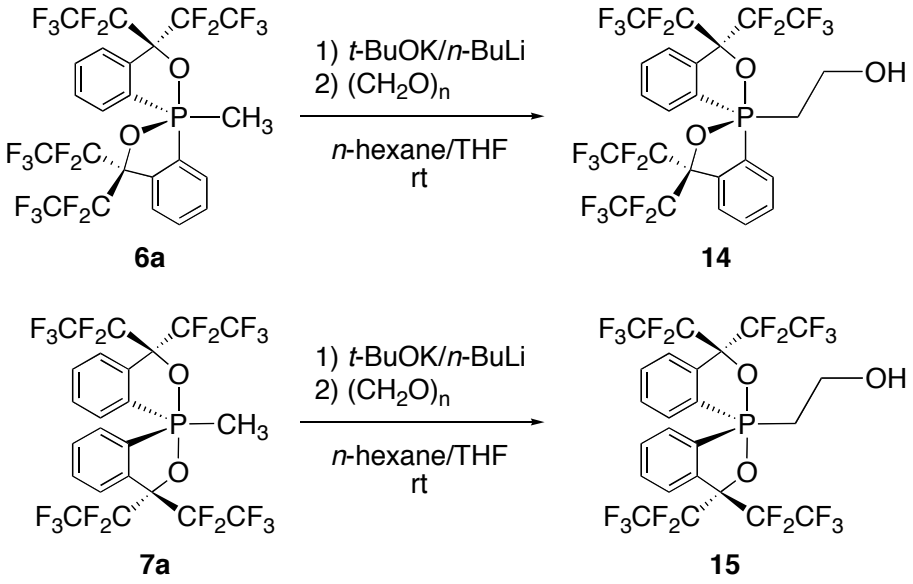
The structures of the pentacoordinate phosphoranes **9a**, **9c**, **9d**, **10b**, **10c** and **10d** were confirmed by X-ray analysis (Figure 3), showing that all the structures were regarded as having a distorted trigonal bipyramidal (TBP) geometry. The selected bond lengths and angles are summarized in Table 4.

Novel conversion of the *O*-apical phosphorane to the *O*-equatorial isomer via hexacoordinate phosphates

We also synthesized an isomeric pair of β-hydroxyethylphosphoranes **14** and **15** by the reaction of the α-carbanion derived from **6a** and **7a** with paraformaldehyde (Scheme 9). The structures of these phosphoranes were confirmed by a single crystal X-ray analysis (Figure 4).

The treatment of **14** and **15** with KH afforded a hexacoordinate phosphate bearing an oxaphosphetane ring **16** (^{31}P NMR: δ = –97.3 ppm in THF) and **17** (–104.4 ppm), respectively. These highly upfield-shifted ^{31}P signals were similar to those of the reported hexacoordinate oxaphosphetane anions.[4,13-15] Surprisingly, when a THF solution of **17** was heated at 60 °C, **17** gradually isomerized to **16** (Scheme 10 and Figure 5). This means that the *O*-apical phosphorane can be converted into the *O*-equatorial isomer under basic conditions. Actually, when a mixture of **15** and KH was heated at 60 °C

for 8.5 h, followed by the addition of NH_4Cl aq., we could obtain the *O*-equatorial phosphorane **14** in 77% yield. As expected, the thermal conversion of **14** to **15** occurred almost quantitatively. These results indicate that **14** and **15** are capable of interconverting with each other in this system.



Scheme 9

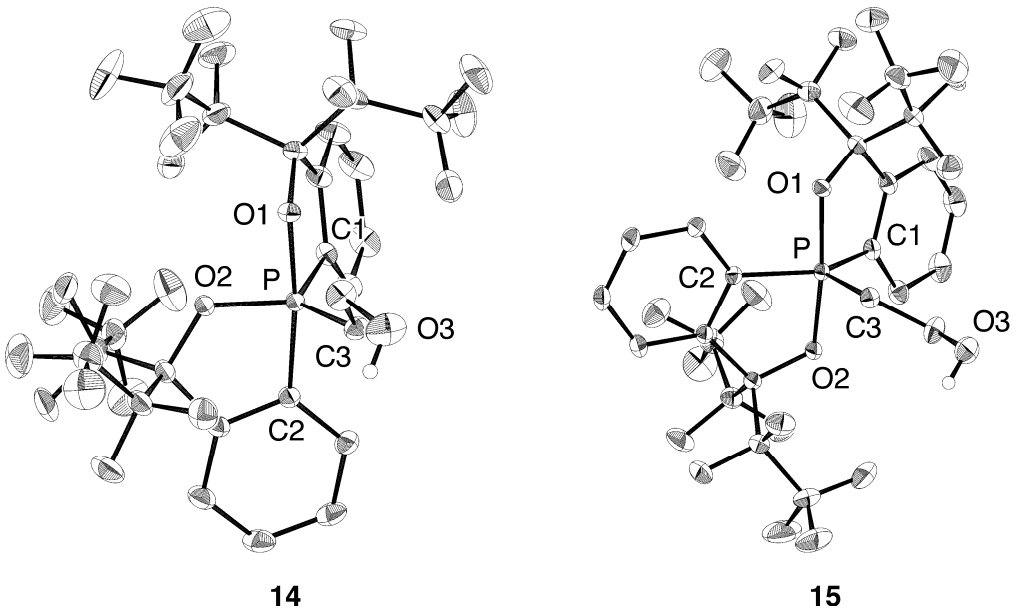


Figure 4. The ORTEP drawings of *β*-hydroxyethylphosphoranes (**14** and **15**) showing the thermal ellipsoids at the 30% probability level. The hydrogen atoms, except for the hydroxyl proton, are omitted for clarity.

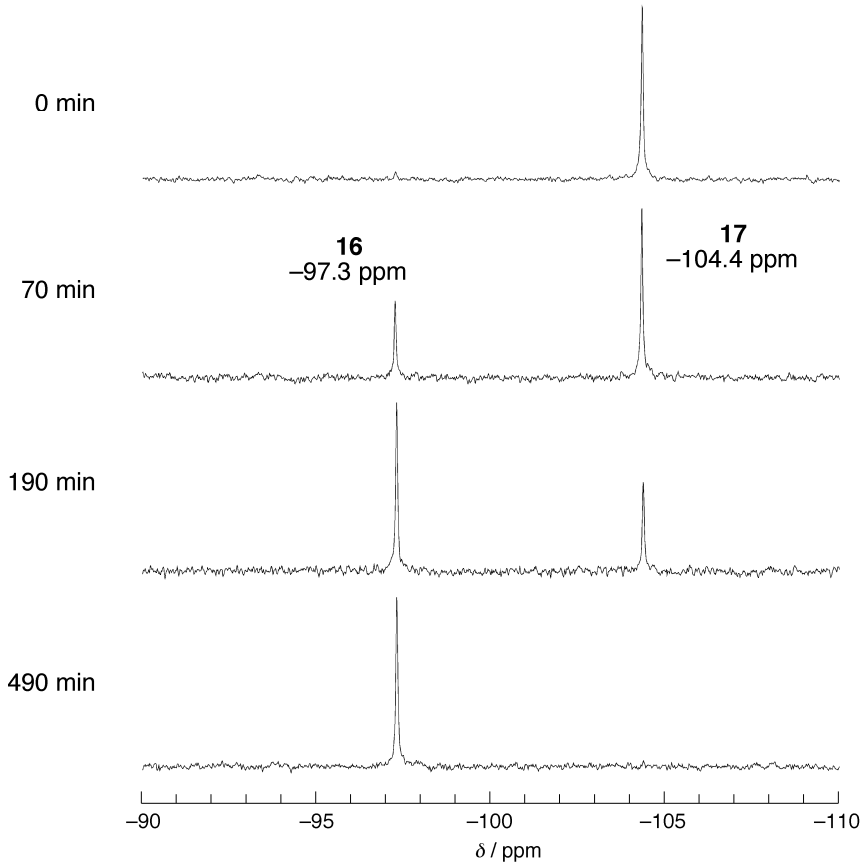
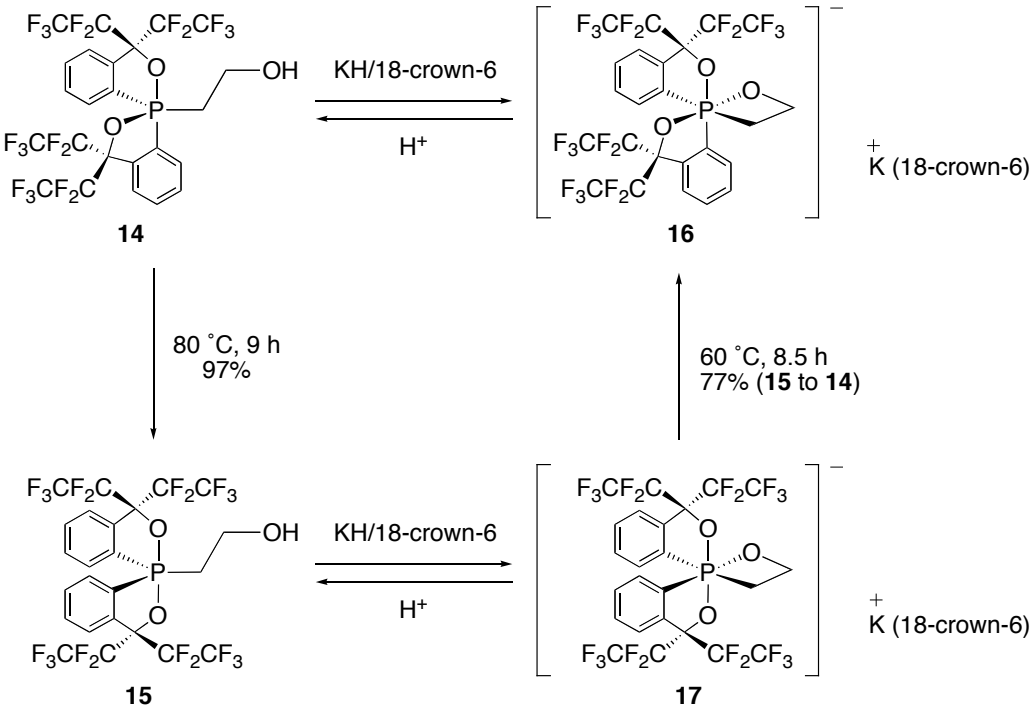
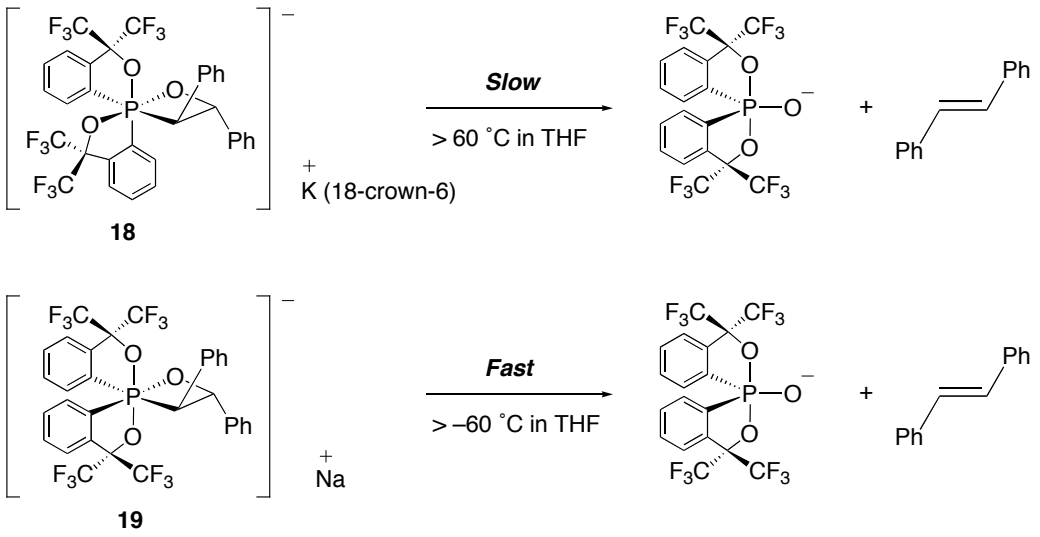


Figure 5. Time course of the ^{31}P NMR for the conversion of **17** to **16** at 60 ˚C in THF.



Scheme 10



Scheme 11

We have already clarified that the *O*-apical phosphoranes are more stable than the *O*-equatorial isomers. All the *O*-equatorial phosphoranes that we isolated so far irreversibly isomerized into the *O*-apical counterparts, and the diffirence in energy was estimated to be more than 12 kcal mol^{-1} for the *n*-butylphosphoranes.[3] On the other hand, as for the stability of the hexacoordinate species, our group have demonstrated that the phosphate **18** derived from the *O*-equatorial phosphorane shows a higher stability toward decomposition than **19** derived from the *O*-apical phosphorane (Scheme 11).[4,15] The phosphate **18** has one oxygen atom trans to the oxygen of the four-membered ring, indicating that the trans influence is highly related to the stability of the phosphates bearing an oxaphosphetane ring. This is in good agreement with the relative stability in the present system (**16** > **17**). Since both **16** and **17** were not thermally decomposed upon heating at 60 ˚C, unlike the case of **18** or **19**, we could directly observe the stereomutation of **17** to **16**, giving rise to determining the thermodynamic relative stability of the two isomeric hexacoordinate phosphates.

In conclusion, we presented some reactions of the *O*-equatorial and *O*-apical spirophosphoranes (**6a** and **7a**). No nucleophilic reaction at the phosphorus atom was observed in both cases. We found that the reaction of **6a** with the Superbase afforded the α-carbanion adjacent to the phosphorus atom (**11-K**), which was treated with some electrophiles ($BrCF_2CF_2Br$, ICH_2CH_2I, and PhSeBr) to produce new phosphorane derivatives. Using the β-hydroxyethylphosphoranes (**14** and **15**), we found a novel interconversion between the *O*-apical and *O*-equatorial phosphoranes. The vequatorial **14** was almost quantitatively converted into the *O*-apical **15** under neutral conditions, whereas the *O*-apical **15** could be converted into the *O*-equatorial **14** in 77% yield under anionic conditions involving the hexacoordinate intermediates **16** and **17**.

EXPERIMENTAL

General.

The melting points were measured using a Yanaco micro melting point apparatus. The ^{1}H NMR (400 MHz), ^{19}F NMR (376 MHz), and ^{31}P NMR (162 MHz) spectra were recorded using a JEOL EX-400 or a JEOL AL-400 spectrometer. The ^{1}H NMR chemical shifts (δ) are given in ppm downfield from Me_4Si, determined by residual chloroform (δ 7.26). The ^{19}F and ^{31}P NMR chemical shifts (δ) are given in ppm downfield from the external $CFCl_3$ and 85% H_3PO_4, respectively. The elemental analyses were performed using a Perkin-Elmer 2400 CHN elemental analyzer. All reactions were carried out under N_2 or Ar. Tetrahydrofuran (THF) and diethyl ether (Et_2O) were freshly distilled from Na-benzophenone, *n*-hexane was distilled over Na, and the other solvents were distilled over CaH_2. Merck silica gel 60 was used for the column chromatography.

Reaction of α-anion of 6a with MeI ~ Synthesis of [*TBPY*-5-12]-1-Ethyl-3,3,3',3'-tetrakis(pentafluoroethyl)-1,1'-spirobi[3*H*,2,1,λ^5-benzoxaphosphole] (9a).

Under N_2, *n*-BuLi (1.56 M *n*-hexane solution, 0.24 mL, 0.37 mmol) was added to a mixture of **6a** (250 mg, 0.34 mmol) and *t*-BuOK (1.0 M THF solution, 0.37 mL, 0.37 mmol) suspended in *n*-hexane (12 mL) at 0 °C. The mixture was then stirred for 1 h at rt. MeI (0.20 mL, 3.21 mmol) was added at 0 °C and the mixture was again stirred for 1 h at rt. The mixture was extracted with ether (2 x 60 mL), and the brown organic layer was washed with brine (2 x 40 mL) and dried over anhydrous $MgSO_4$. After removing the solvents by evaporation, the crude mixture was separated by column chromatography (CH_2Cl_2 : *n*-hexane = 1 : 4), followed by reversed-phase HPLC (MeCN) to afford **9a** (RT = 28.8 min.: 79.6 mg, 31%) as a white solid. The colorless crystals of **9a** suitable for X-ray analysis were obtained by recrystallization from CH_3CN: mp 98.7-99.3 °C (decomp); ^{1}H NMR ($CDCl_3$) δ = 7.79-7.74 (m, 4H, aromatic), 7.64-7.57 (m, 4H, aromatic), 2.46 (dq, $^{2}J_{H\text{-}P}$ = 19, $^{3}J_{H\text{-}H}$ = 8 Hz, 2H, PCH_2), 1.13 (dt, $^{3}J_{H\text{-}P}$ = 24, $^{3}J_{H\text{-}H}$ = 8 Hz, 3H, CH_3); ^{19}F NMR ($CDCl_3$) δ = –79.1 (s, 12F, CF_2CF_3), –115.6 (br s, 4F, CF_2CF_3), –116.3 (br s, 4F, CF_2CF_3); ^{31}P NMR ($CDCl_3$) δ = –0.5; Anal. Calcd for $C_{24}H_{13}F_{20}O_2P$: C, 38.73; H, 1.76. Found: C, 39.05; H, 1.71.

Reaction of α-anion of 6a with $BrCF_2CF_2Br$ ~ Synthesis of [*TBPY*-5-11]-1-Bromomethyl-3,3,3',3'-tetrakis(pentafluoroethyl)-1,1'-spirobi[3*H*,2,1,λ^5-benzoxaphosphole] (10b).

To an α-anion prepared from **6a** (29.7 mg, 0.040 mmol) by the above-described procedure was added $BrCF_2CF_2Br$ (0.02 mL, 0.16 mmol) at –78 °C. The mixture was stirred for 1 h at rt. The mixture was extracted with ether (2 x 40 mL), and the brown organic layer was washed with brine (2 x 30 mL) and dried over anhydrous $MgSO_4$. After removing the solvents by evaporation, the resulting crude was

separated by TLC (CH_2Cl_2 : *n*-hexane = 1 : 4) to afford **10b** (16.5 mg, 50%) as a white solid. The colorless crystals of **10b** suitable for X-ray analysis were obtained by recrystallization from CH_2Cl_2/*n*-hexane: mp 141.0-141.6 °C; ^{1}H NMR ($CDCl_3$) δ = 8.50-8.46 (m, 2H, aromatic), 7.78 (br s, 2H, aromatic), 7.76-7.68 (m, 4H, aromatic), 3.65 (dd, $^2J_{P\text{-}H}$ = 6.6 Hz, $^2J_{H\text{-}H}$ = 11.2 Hz, 1H, PC*H*$_2$Br), 3.54 (dd, $^2J_{P\text{-}H}$ = 6.6 Hz, $^2J_{H\text{-}H}$ = 11.2 Hz, 1H, PC*H*$_2$Br); ^{19}F NMR ($CDCl_3$) δ = –78.4 (s, 6F, CF_2CF_3), –79.4 (dd, $^3J_{F\text{-}F}$ = 19 Hz, $^5J_{F\text{-}F}$ = 6 Hz, 6F, CF_2CF_3), –116.4 (dq, $^2J_{F\text{-}F}$ = 287 Hz, $^3J_{F\text{-}F}$ = 19 Hz, 2F, CF_2CF_3), –116.6 (s, 2F, CF_2CF_3), –116.7 (s, 2F, CF_2CF_3), –121.4 (dm, $^2J_{F\text{-}F}$ = 287 Hz, 2 F, CF_2CF_3); ^{31}P NMR ($CDCl_3$) δ = –22.7. MS (EI(+)): *m*/*z* = 807 $[M]^+$, 808 $[M+1]^+$, 809 $[M+2]^+$, 715 $[M–CH_2Br]^+$; Anal. Calcd for $C_{23}H_{10}F_{20}BrO_2P$: C, 34.14; H, 1.25. Found: C, 34.35; H, 1.35.

Reaction of α-anion of 6a with ICH_2CH_2I ~ Synthesis of [*TBPY*-5-12]-1-Iodomethyl-3,3,3',3'-tetrakis(pentafluoroethyl)-1,1'-spirobi[3*H*,2,1,λ^5-benzoxaphosphole] (9c) and [*TBPY*-5-11]-1-Iodomethyl-3,3,3',3'-tetrakis(pentafluoroethyl)-1,1'-spirobi[3*H*,2,1,λ^5-benzoxaphosphole] (10c).

To an α-anion prepared from **6a** (183 mg, 0.251 mmol) by the above-described procedure was added ICH_2CH_2I (284 mg, 1.0 mmol) at 0 °C. The mixture was stirred for 2 h at 0 °C. The mixture was extracted with *n*-hexane cooled to 0 °C (2 x 60 mL), and the brown organic layer was washed with brine cooled to 0 °C (2 x 40 ml) and dried over anhydrous $MgSO_4$. After filtering the organic layer through SiO_2 and removing the solvents by evaporation at 0 °C, the residue was separated by reversed-phase HPLC (CH_3CN) at rt to afford **9c** (RT = 30.4 min.: 113 mg, 52%) and **10c** (RT = 36.8 min.: 10.8 mg, 5%) as white solids. The colorless crystals of **9c** and **10c** suitable for X-ray analysis were obtained by recrystallization from *n*-hexane. **9c**: mp 85.6-86.4 °C (decomp); ^{1}H NMR ($CDCl_3$) δ = 8.20 (br s, 2H, aromatic), 7.78-7.59 (m, 6H, aromatic), 3.51 (br s, 2H, PC*H*$_2$I); ^{19}F NMR ($CDCl_3$) δ = –79.1 (s, 12F, CF_2CF_3), –115.1 (br s, 4F, CF_2CF_3), –115.9 (br s, 4F, CF_2CF_3); ^{31}P NMR ($CDCl_3$) δ = –8.0; Anal. Calcd for $C_{23}H_{10}F_{20}IO_2P$: C, 32.27; H, 1.18. Found: C, 31.95; H, 1.14. **10c**: mp 107.0-107.7 °C ; ^{1}H NMR ($CDCl_3$) δ = 8.51-8.43 (m, 2H, aromatic), 7.80-7.72 (m, 6H, aromatic), 3.53 (dd, $^2J_{H\text{-}P}$ = 8, $^2J_{H\text{-}H}$ = 11 Hz, 1H, PC*H*$_2$I), 3.37 (dd, $^2J_{H\text{-}P}$ = 4, $^2J_{H\text{-}H}$ = 11 Hz, 1H, PC*H*$_2$I); ^{19}F NMR ($CDCl_3$) δ = –78.5 (s, 6F, CF_2CF_3), –79.2 (dd, $^3J_{F\text{-}F}$ = 19.7 Hz, $^5J_{F\text{-}F}$ = 7.4 Hz, 6F, CF_2CF_3), –116.4 (dq, $^2J_{F\text{-}F}$ = 288 Hz, $^3J_{F\text{-}F}$ = 19.7 Hz, 2F, CF_2CF_3), –116.4 (s, 2F, CF_2CF_3), –116.5 (s, 2F, CF_2CF_3), –121.3 (dq, $^2J_{F\text{-}F}$ = 288 Hz, $^5J_{F\text{-}F}$ = 7.4 Hz, 2F, CF_2CF_3); ^{31}P NMR ($CDCl_3$) δ = –22.5; Anal. Calcd for $C_{23}H_{10}F_{20}IO_2P$: C, 32.27; H, 1.18. Found: C, 31.96; H, 1.09.

Reaction of α-anion of 6a with PhSeBr ~ Synthesis of [*TBPY*-5-12]-1-Phenylselenomethyl-

3,3,3',3'-tetrakis(pentafluoroethyl)-1,1'-spirobi[3*H*,2,1,λ^5-benzoxaphosphole] (9d) and [*TBPY*-5-11]-1-Phenylselenomethyl-3,3,3',3'-tetrakis(pentafluoroethyl)-1,1'-spirobi[3*H*,2,1,λ^5-benzoxaphosphole] (10d).

To an α-anion prepared from **6a** (102.8 mg, 0.141 mmol) by the above-described procedure was added PhSeBr (129.6 mg, 0.538 mmol) at 0 °C. The mixture was stirred for 2.5 h at rt. The mixture was extracted with Et_2O (2 x 50 mL), and the brown organic layer was washed with brine (2 x 40 mL) and dried over anhydrous $MgSO_4$. After filtering the organic layer through SiO_2 and removing the solvents by evaporation, the residue was separated by reversed-phase HPLC (MeCN) to afford **9d** (RT = 31 min.: 22.4 mg, 0.0253 mmol, 18%) and **10d** (RT = 38.6 min.: 18.5 mg, 0.0208 mmol, 14%) as white solids. The colorless crystals of **9d** and **10d** suitable for X-ray analysis were obtained by recrystallization from *n*-hexane and $CHCl_3$, respectively. **9d**: mp 94.1-95.0 °C (decomp); ^{1}H NMR ($CDCl_3$) δ = 8.03 (t, $^3J_{H\text{-}H}$ = 8 Hz, 2H, aromatic), 7.75 (br d, $^3J_{H\text{-}H}$ = 8 Hz, 2H, aromatic), 7.64 (t, $^3J_{H\text{-}H}$ = 8 Hz, 2H, aromatic), 7.55 (d, $^3J_{H\text{-}H}$ = 8 Hz, 2H, aromatic), 7.51 (d, $^3J_{H\text{-}H}$ = 8 Hz, 2H, aromatic), 7.28-7.26 (m, 1H, aromatic), 7.19 (dd, $^3J_{H\text{-}H}$ = 8 Hz, $^4J_{H\text{-}H}$ = 2 Hz, 2H, aromatic), 3.64 (br d, $^3J_{H\text{-}P}$ = 11 Hz, 2H, PCH_2Se); ^{19}F NMR ($CDCl_3$) δ = –78.8 (s, 6F, CF_2CF_3), –79.0 (s, 6F, CF_2CF_3), –115.3 (br s, 4F, CF_2CF_3), –116.1 (br s, 4F, CF_2CF_3); ^{31}P NMR ($CDCl_3$) δ = –6.3. **10d**: mp 97.0-98.0 °C; ^{1}H NMR ($CDCl_3$) δ = 8.51 (m, 2H, aromatic), 7.76-7.71 (m, 6H, aromatic), 7.25-7.23 (m, 1H, aromatic), 7.16-7.10 (m, 4H, aromatic), 3.56 (dd, $^2J_{H\text{-}P}$ = 12, $^2J_{H\text{-}H}$ = 12 Hz, 1H, PCH_2Se), 3.29 (dd, $^2J_{H\text{-}P}$ = 8, $^2J_{H\text{-}H}$ = 12 Hz, 1H, PCH_2Se); ^{19}F NMR ($CDCl_3$) δ = –78.5 (s, 6F, CF_2CF_3), –79.3 (dd, $^3J_{F\text{-}F}$ = 19.9 Hz, $^5J_{F\text{-}F}$ = 7.5 Hz, 6F, CF_2CF_3), –116.5 (dq, $^2J_{F\text{-}F}$ = 288 Hz, $^3J_{F\text{-}F}$ = 19.9 Hz, 2F, CF_2CF_3), –116.6 (s, 2F, CF_2CF_3), –116.7 (s, 2F, CF_2CF_3), –121.3 (dq, $^2J_{F\text{-}F}$ = 288 Hz, $^5J_{F\text{-}F}$ = 7.5 Hz, 2F, CF_2CF_3); ^{31}P NMR ($CDCl_3$) δ = –20.5; Anal. Calcd for $C_{29}H_{15}F_{20}O_2PSe$: C, 39.34; H, 1.71. Found: C, 39.42; H, 1.69.

Synthesis of *O*-equatorial 14 ([*TBPY*-5-12]-1-(2-Hydroxyethyl)-3,3,3',3'-tetrakis(pentafluoroethyl)-1,1'-spirobi[3*H*,2,1,λ^5-benzoxaphosphole]).

To an α-anion prepared from **6a** (374 mg, 0.513 mmol) by the above-described procedure was added paraformaldehyde (64 mg, 2.0 mmol) at 0 °C. The mixture was stirred for 21 h at rt. The reaction was quenched with aqueous NH_4Cl (50 mL). The mixture was extracted with Et_2O (2 x 80 mL), and the brown organic layer was washed with brine (2 x 50 mL) and dried over anhydrous $MgSO_4$. After filtering the organic layer through SiO_2 and removing the solvents by evaporation, the resulting crude mixture was separated by reversed-phase HPLC (MeCN) to afford **14** (RT = 41 min.: 275 mg, 70%) as a white solid. The colorless crystals of **14** suitable for X-ray analysis were obtained by recrystallization from *n*-hexane/CH_2Cl_2: mp 112.0-112.9 °C (decomp); ^{1}H NMR ($CDCl_3$) δ = 7.78-7.74 (m, 4H, aromatic), 7.65-7.57 (m, 4H, aromatic), 3.89 (dt, $^2J_{H\text{-}P}$ = 17, $^3J_{H\text{-}H}$ = 8 Hz, 2H, PCH_2), 2.75 (br s, 2H, PCH_2CH_2); ^{19}F

NMR ($CDCl_3$) δ = –78.9 (s, 6F, CF_2CF_3), –79.4 (s, 6F, CF_2CF_3), –116.1 (br d, $^2J_{F\text{-}F}$ = 290 Hz, 4F, CF_2CF_3), –117.4 (br d, $^2J_{F\text{-}F}$ = 290 Hz, 4F, CF_2CF_3); ^{31}P NMR ($CDCl_3$) δ = –2.8; Anal. Calcd for $C_{24}H_{13}F_{20}O_3P$: C, 37.91; H, 1.72. Found: C, 37.76; H, 1.77.

Synthesis of *O*-apical 15 ([*TBPY*-5-11]-1-(2-Hydroxyethyl)-3,3,3',3'-tetrakis(pentafluoroethyl)-1,1'-spirobi[3*H*,2,1,λ^5-benzoxaphosphole]).

To an α-anion prepared from **7a** (118 mg, 0.162 mmol) by the above-described procedure was added paraformaldehyde (29 mg, 0.91 mmol) at 0 °C. The mixture was stirred for 2 h at rt. The reaction was quenched with aqueous NH_4Cl (30 mL). The mixture was extracted with Et_2O (2 x 50 mL), and the brown organic layer was washed with brine (2 x 30 mL) and dried over anhydrous $MgSO_4$. After filtering the organic layer through SiO_2 and removing the solvents by evaporation, the resulting crude mixture was separated by reversed-phase HPLC (MeCN) to afford **15** (RT = 24 min.: 38.1 mg, 30%) as a white solid. The colorless crystals of **15** suitable for X-ray analysis were obtained by recrystallization from *n*-hexane: mp 146.6-147.6 °C; ^{1}H NMR ($CDCl_3$) δ = 8.46-8.41 (m, 2H, aromatic), 7.77-7.68 (m, 6H, aromatic), 3.91-3.87 (m, 1H, PCH_2), 3.45-3.41 (m, 1H, PCH_2), 2.51-2.42 (m, 2H, PCH_2CH_2); ^{19}F NMR ($CDCl_3$) δ = –78.4 (s, 6F, CF_2CF_3), –79.5 (dd, $^3J_{F\text{-}F}$ = 19, $^5J_{F\text{-}F}$ = 6 Hz, 6F, CF_2CF_3), –116.4 (dq, $^2J_{F\text{-}F}$ = 290, $^3J_{F\text{-}F}$ = 19 Hz, 2F, CF_2CF_3), –117.2 (d, $^2J_{F\text{-}F}$ = 290 Hz, 4F, CF_2CF_3), –121.1 (dm, $^2J_{F\text{-}F}$ = 290 Hz, 2F, CF_2CF_3); ^{31}P NMR ($CDCl_3$) δ = –21.5; Anal. Calcd for $C_{24}H_{13}F_{20}O_3P$: C, 37.91; H, 1.72; Found: C, 37.95; H, 1.71.

Synthesis of hexacoordinate phosphate 16.

A THF (0.6 mL) solution of **14** (12.2 mg, 0.016 mmol) and 18-crown-6 ether (7.5 mg, 0.028 mmol) was added to a THF (0.6 mL) suspension of KH (excess), then the mixture was stirred for 10 min at 0 °C. After removing the THF in vacuo, dry CD_3CN (0.6 mL) was added. The solution was transferred to an NMR tube under N_2, and the NMR spectra of **16** were recorded. ^{1}H NMR (CD_3CN) δ = 8.05 (t, $^3J_{H\text{-}H}$ = 6.8 Hz, 1H, aromatic), 7.52 (tdd, $^3J_{H\text{-}H}$ = 6.8, $^4J_{H\text{-}P}$ = 2.4, $^4J_{H\text{-}H}$ = 1.2 Hz, 2H, aromatic) 7.35-7.40 (m, 2H, aromatic), 7.12 (tdd, $^3J_{H\text{-}H}$ = 6.8, $^4J_{H\text{-}P}$ = 2.4, $^3J_{H\text{-}H}$ = 1.2 Hz, 1H, aromatic), 6.94 (dd, $^3J_{H\text{-}P}$ = 12.9, $^3J_{H\text{-}H}$ = 6.8 Hz, 1H, aromatic), 6.53 (dd, $^3J_{H\text{-}P}$ = 13.9, $^3J_{H\text{-}H}$ = 6.8 Hz, 1H, aromatic), 3.56 (br s, 24H, 18-crown-6), 3.35-3.42 (m, 2H, PCH_2), 2.03-2.12 (m, 2H, PCH_2CH_2); ^{19}F NMR (CD_3CN) δ = –76.9 (br d, $^3J_{F\text{-}F}$ = 18.4 Hz, 3F, CF_2CF_3), –77.3 (br s, 3F, CF_2CF_3), –75.5 (br s, 3F, CF_2CF_3), –77.8 (dd, $^3J_{F\text{-}F}$ = 18.4, $^5J_{F\text{-}F}$ = 9.8 Hz, 3F, CF_2CF_3), –109.3 (d, $^2J_{F\text{-}F}$ = 290 Hz, 1F, CF_2CF_3), –109.5 (br d, $^2J_{F\text{-}F}$ = 290 Hz, 1F, CF_2CF_3), –112.6 (d, $^2J_{F\text{-}F}$ = 290 Hz, 1F, CF_2CF_3), –112.7 (d, $^2J_{F\text{-}F}$ = 290 Hz, 1F, CF_2CF_3), –113.2 (ddq, $^2J_{F\text{-}F}$ = 290, $^4J_{F\text{-}F}$ = 18.4, $^3J_{F\text{-}F}$ = 18.4 Hz, 1F, CF_2CF_3), –113.8 (dm, $^2J_{F\text{-}F}$ = 290 Hz, 1F, CF_2CF_3), –114.7 (dm, $^2J_{F\text{-}F}$ = 290 Hz, 1F, CF_2CF_3), –114.9 (ddq, $^2J_{F\text{-}F}$ = 290, $^4J_{F\text{-}F}$ = 18.4, $^5J_{F\text{-}F}$ = 9.8 Hz, 1 F, CF_2CF_3); ^{31}P NMR (CD_3CN): δ = –98.2.

Synthesis of hexacoordinate phosphate 17.

A THF (0.6 mL) solution of **15** (20.0 mg, 0.027 mmol) and 18-crown-6 ether (8.8 mg, 0.033 mmol) was added to a THF (0.6 mL) suspension of KH (excess), then the mixture was stirred for 10 min at 0 °C. After removing the THF in vacuo, dry CD_3CN (0.6 mL) was added. The solution was transferred to an NMR tube under N_2, and the NMR spectra of **17** were recorded. ^{1}H NMR (CD_3CN) δ = 7.95 (dd, $^3J_{H\text{-}P}$ = 12.4, $^3J_{H\text{-}H}$ = 7.2 Hz, 1H, aromatic), 7.75 (dd, $^3J_{H\text{-}P}$ = 12.9, $^3J_{H\text{-}H}$ = 7.2 Hz, 1H, aromatic), 7.45 (br s, 2H, aromatic), 7.35-7.42 (m, 2H, aromatic), 7.24-7.29 (m, 2H, aromatic), 3.56 (br s, 24H, 18-crown-6), 3.13-3.25 (m, 2H, PCH_2), 2.05-2.13 (m, 2H, PCH_2CH_2); ^{19}F NMR (CD_3CN) δ = –78.3 - –78.4 (m, 3F, CF_2CF_3), –78.7 - –78.8 (m, 3F, CF_2CF_3), –79.3 - –79.4 (m, 3F, CF_2CF_3), –79.6 - –79.7 (m, 3F, CF_2CF_3), –108.8 (d, $^2J_{F\text{-}F}$ = 290 Hz, 1F, CF_2CF_3), –109.4 (d, $^2J_{F\text{-}F}$ = 290 Hz, 1F, CF_2CF_3), –113.6 (dm, $^2J_{F\text{-}F}$ = 290 Hz, 4F, CF_2CF_3), –114.4 (d, $^2J_{F\text{-}F}$ = 290 Hz, 2F, CF_2CF_3); ^{31}P NMR (CD_3CN) δ = –105.2.

Synthesis of 15 from 14 under neutral conditions.

A C_6D_6 (0.5 mL) solution of **14** (14.0 mg, 0.0184 mmol) was heated at 80 °C for 9 h. After concentration in vacuo, **15** was obtained (13.6 mg, 97%) as a white solid. The spectral data were consistent with those of the product obtained in the synthesis of **15**.

Synthesis of 14 from 15 under anionic conditions.

A THF (0.6 mL) solution of **15** (35.7 mg, 0.0469 mmol) and 18-crown-6 ether (12.4 mg, 0.0469 mmol) was added to a THF (0.5 mL) suspension of KH (excess), then the mixture was stirred for 10 min at 0 °C. The supernatant was transferred to an NMR tube under N_2, and the mixture was heated for 8.5 h at 60 ˚C. The reaction was monitored by ^{31}P NMR. The mixture was treated with aqueous NH_4Cl (10 mL). The mixture was extracted with Et_2O (2 × 20 mL) and the organic layer was washed with brine (2 × 20 mL) and dried over anhydrous $MgSO_4$. After removing the solvents by evaporation, the resulting crude was separated by column chromatography (CH_2Cl_2 : *n*-hexane = 1 : 3) to afford **14** (27.7 mg, 77%) as a white solid. The spectral data were consistent with those of the same product obtained as the product in the synthesis of **14**.

Single crystal X-ray analysis of 9a, 9c, 9d, 10b, 10c, 10d, 14 and 15.

Crystals suitable for the X-ray structural determination were mounted on a Mac Science DIP2030 imaging plate diffractometer and irradiated with graphite monochromated Mo-*K*α radiation (λ = 0.71073 Å) for the data collection. The unit cell parameters were determined by separately autoindexing several images in each data set using the DENZO program (MAC Science).[16] For each data set, the rotation

images were collected in 3 degree increments with a total rotation of 180 deg about the ϕ axis. The data were processed using SCALEPACK. The structure was solved by a direct method with the SHELX-97 program.[17] Refinement on F^2 was carried out using the full-matrix leat-squares by the SHELX-97 program.[17] All non-hydrogen atoms were refined using the anisotropic thermal parameters. The hydrogen atoms were included in the refinement along with the isotropic thermal parameters. The crystallographic data are summarized in Table 5.

CCDC-652179 (**9a**), 652180 (**9c**), 652181 (**9d**), 652182 (**10b**), 652183 (**10c**), 652184 (**10d**), 652185 (**14**) and 652186 (**15**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table 5. Crystallographic data for **9a**, **9c**, **9d**, **10b**, **10c**, **10d**, **14** and **15**.

Compound	**9a**	**9c**	**9d**	**10b**
Formula	$C_{24}H_{13}F_{20}O_2P$	$C_{23}H_{10}F_{20}IO_2P$	$C_{29}H_{15}F_{20}O_2PSe$	$C_{23}H_{10}F_{20}BrO_2P$
Mol wt	744.31	856.18	885.34	809.19
Cryst syst	monoclinic	monoclinic	monoclinic	orthorhombic
Space group	$P2_1/c$	$P2_1/a$	$P2_1/c$	$Pbcn$
Color	colorless	colorless	colorless	colorless
Habit	plate	plate	plate	plate
Cryst dimens, mm	0.40 x 0.40 x 0.20	0.30 x 0.30 x 0.10	0.50 x 0.50 x 0.15	0.50 x 0.30 x 0.20
a, Å	9.3210(2)	9.7040(3)	20.2180(3)	18.6030(8)
b, Å	17.5280(3)	14.6860(5)	8.3780(10)	8.6890(2)
c, Å	16.8660(4)	19.6440(8)	20.9830(6)	17.1930(6)
α, deg	90	90	90	90
β, deg	95.6980(10)	95.3130(10)	117.6400(10)	90
γ, deg	90	90	90	90
V, Å^3	2741.93(10)	2787.50(17)	3148.62(11)	2779.10(17)
Z	4	4	4	4
D_{calc}, g cm^{-3}	1.803	2.040	1.868	1.934
Abs coeff, mm^{-1}	0.261	1.364	1.392	1.695
F(000)	1472	1648	1736	1576
Radiation; λ, Å	Mo Kα, 0.71073	Mo Kα, 0.71073	Mo Kα, 0.71073	Mo Kα, 0.71073
Temp, K	298(2)	298(2)	298(2)	298(2)
Data, collcd	$+h, +k, \pm l$	$+h, +k, \pm l$	$+h, +k, \pm l$	$+h, +k, +l$
Data/restrains/param	6080/0/425	6177/0/424	7007/0/478	3111/0/218
R_1 [$I > 2\sigma(I)$]	0.0655	0.0548	0.0629	0.0780
wR_2 (all data)	0.2275	0.2151	0.2117	0.2865
GOF	1.076	1.196	1.104	1.175
Solv for crystallization	CH_3CN	n-hexane	CH_3CN	CH_2Cl_2/n-hexane

Compound	**10c**	**10d**	**14**	**15**
Formula	$C_{23}H_{10}F_{20}IO_2P$	$C_{29}H_{15}F_{20}O_2PSe$	$C_{24}H_{13}F_{20}O_3P$	$C_{24}H_{13}F_{20}O_3P$
Mol wt	856.18	885.34	760.31	760.31
Cryst syst	triclinic	monoclinic	monoclinic	monoclinic
Space group	*P*–1	$P2_1/n$	$P2_1/c$	$P2_1/c$
Color	colorless	colorless	colorless	colorless
Habit	plate	plate	plate	plate
Cryst dimens, mm	0.35 x 0.20 x 0.15	0.60 x 0.40 x 0.15	0.50 x 0.40 x 0.30	0.40 x 0.25 x 0.20
a, Å	9.8110(2)	13.2410(3)	8.7220(2)	9.79100(10)
b, Å	9.8770(3)	13.4470(4)	17.0420(3)	19.2970(4)
c, Å	15.1740(5)	18.9800(5)	18.4890(3)	14.4780(4)
α, deg	82.7890(10)	90	90	90
β, deg	81.2620(10)	107.6330(2)	94.5790(10)	95.0350(10)
γ, deg	79.243(2)	90	90	90
V, Å^3	1420.64(7)	3220.64(15)	2739.44(9)	2724.87(10)
Z	2	4	4	4
D_{calc}, g cm^{-3}	2.002	1.826	1.843	1.853
Abs coeff, mm^{-1}	1.338	1.361	0.266	0.267
F(000)	824	1736	1504	1504
Radiation; λ, Å	Mo Kα, 0.71073	Mo Kα, 0.71073	Mo Kα, 0.71073	Mo Kα, 0.71073
Temp, K	298(2)	298(2)	298(2)	298(2)
Data, collcd	$+h, \pm k, \pm l$	$+h, +k, \pm l$	$+h, +k, \pm l$	$+h, +k, \pm l$
Data/restrains/param	6047/0/424	7520/0/478	6530/0/434	6227/0/434
R_1 [$I > 2\sigma(I)$]	0.0497	0.0734	0.0467	0.0458
wR_2 (all data)	0.1561	0.2348	0.1716	0.1313
GOF	1.098	1.144	1.154	1.019
Solv for crystallization	*n*-hexane	$CHCl_3$	CH_2Cl_2/*n*-hexane	*n*-hexane

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REFERENCES AND NOTES

1. K.-y. Akiba, 'Chemistry of Hypervalent Compounds', Wiley-VCH, New York, 1999.
2. For the *N*-X-*L* designation, see: C. W. Perkins, J. C. Martin, A. J. Arduengo, W. Lau, A. Alegria, and J. K. Kochi, *J. Am. Chem. Soc.*, 1980, **102**, 7753.
3. S. Kojima, K. Kajiyama, M. Nakamoto, and K.-y. Akiba, *J. Am. Chem. Soc.*, 1996, **118**, 12866; S. Kojima, K. Kajiyama, M. Nakamoto, S. Matsukawa, and K.-y. Akiba, *Eur. J. Org. Chem.*, 2006, 218.
4. S. Matsukawa, S. Kojima, K. Kajiyama, Y. Yamamoto, and K.-y. Akiba, *J. Am. Chem. Soc.*, 2002, **124**, 13154.
5. X.-D. Jiang, K.-i. Kakuda, S. Matsukawa, H. Yamamichi, S. Kojima, and Y. Yamamoto, *Chem.*

Asian J., 2007, **2**, 314.

6. X.-D. Jiang, S. Matsukawa, H. Yamamichi, and Y. Yamamoto, *Inorg. Chem.,* 2007, **46**, 5480.
7. M. Schlosser and J. Hartmann, *Angew. Chem., Int. Ed. Engl.,* 1973, **12**, 508.
8. When a mixture of **6a** and Superbase was treated with D_2O, rather complex mixture was obtained. Therefore, we used MeI as the electrophile.
9. L. Pauling, 'The Nature of the Chemical Bond, 3rd ed', Cornell University, Ithaca, NY, 1960.
10. Inamoto et al. determined the group electronegativity of SePh (2.407): N. Inamoto and S. Masuda, *Chem. Lett.,* 1982, 1003.
11. M. Nakamoto, S. Kojima, S. Matsukawa, Y. Yamamoto, and K.-y. Akiba, *J. Organometal. Chem.,* 2002, **643-644**, 441.
12. T. Adachi, S. Matsukawa, M. Nakamoto, K. Kajiyama, S. Kojima, Y. Yamamoto, K.-y. Akiba, S. Re, and S. Nagase, *Inorg. Chem.,* 2006, **45**, 7269.
13. S. Kojima and K.-y. Akiba, *Tetrahedron Lett.,* 1997, **38**, 547.
14. T. Kawashima, K. Watanabe, and R. Okazaki, *Tetrahedron Lett.,* 1997, **38**, 551.
15. S. Kojima, K. Kawaguchi, and K.-y. Akiba, *Tetrahedron Lett.,* 1997, **38**, 7753; S. Kojima, K. Kawaguchi, S. Matsukawa, and K.-y. Akiba, *Tetrahedron,* 2003, **59**, 255.
16. Z. Otwinowski and W. Minor, Methods in Enzymology, Vol. 276: Macromolecular Crystallography, part A, pp. 307-326, 1997, ed. by C. W. Carter Jr. and R. M. Sweet, Academic Press.
17. G. M. Sheldrick, *SHELX-97*; University of Göttingen: Göttingen, Germany, 1997.