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Synthesis and Application of a Bidentate Ligand Based on Decafluoro-3-phenyl-3-pentanol: Steric Effect of Pentafluoroethyl Groups on the Stereomutation of O-Equatorial C-Apical Spirophosphoranes

Xin-Dong Jiang,[a] Ken-ichiro Kakuda,[a] Shiro Matsukawa,[b] Hideaki Yamamichi,[a] Satoshi Kojima,[a] and Yohsuke Yamamoto*[a]

Abstract: 1,1,1,2,2,4,4,5,5,5-Decafluoro-3-phenyl-3-pentanol was prepared by a Cannizzaro-type disproportionation reaction, and the dimetallated compound was used as a bidentate ligand, which is bulkier than the Martin ligand (1,1,1,3,3,3-hexafluoro-2-phenyl-2-propanol). A P–H spirophosphorane was synthesized by utilizing the new bidentate ligand, and the structure of the product was essentially the same as that of the P–H phosphorane with Martin ligands. Phosphoranes that exhibit reversed apicophilicity (O-equatorial) were also synthesized and could be converted into the corresponding stable stereoisomers (O-apical). The crystal structures of O-equatorial phosphoranes and the O-apical isomers were slightly affected by the steric repulsion of pentafluoroethyl groups. Kinetic measurements revealed that the stereomutation of O-equatorial methylphosphorane to the O-apical isomer was slowed. The activation enthalpy for the stereomutation of the former to the latter was higher than that of the phosphorane with Martin ligands by 5.1 kcal mol^{-1}.

Keywords: hypervalent compounds · isomerization · spiro compounds · steric hindrance · X-ray diffraction

Introduction

Hypervalent phosphorus compounds[1] have attracted great interest because such species are assumed to be involved as intermediates (or transition states) in the biological phosphoryl transfer reaction.[2] According to the Westheimer rule,[2d] in phosphoryl transfer reactions, a nucleophile attacks a phosphoryl center to give a pentacoordinate intermediate that bears the nucleophile at the apical position, then one of the two apical ligands is released to be a nucleofuge. During this reaction, if the intermediate is sufficiently long-lived, it can easily undergo stereomutation to furnish an equilibrium mixture containing several stereoisomers; this can highly affect the product distribution. Thus, to clarify the mechanism of such reactions, comprehensive knowledge of the thermodynamic and kinetic properties of transient species would be needed; therefore, it is quite important to understand the difference in structure and reactivity of isomeric phosphoranes.

Pentacoordinate (10-P-5)[3] phosphoranes generally prefer a trigonal-bipyramidal (TBP) structure, which bears two distinct bonds (apical and equatorial). The apical bond is described as a three-center-four-electron (hypervalent) bond, whereas the equatorial bond is described as an sp^2 bond. Because of the distinct sites and bonds existing in the TBP structure, two characteristic properties, apicophilicity (a thermodynamic property) and pseudorotation (a kinetic property), play important roles in hypervalent phosphorane chemistry. Apicophilicity is the relative preference of a ligand to occupy the apical site, and many experimental studies[4] and theoretical calculations[5] have clarified that electronegative and sterically small groups prefer to occupy the apical sites, whereas electron-donating and bulky ligands prefer the equatorial sites. However, TBP molecules generally isomerize in solution by a mechanism called Berry pseudorotation (BPR),[6] which causes rapid exchange between the apical and equatorial ligands.[7] The barrier to BPR is

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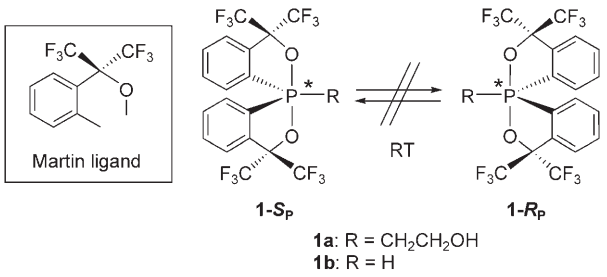
usually very low (calculated to be $\approx$2–3 kcal mol^{-1} for PH_5[8]) without any steric restrictions.

It has been found that the Martin ligand, which forms a rigid five-membered ring, stabilizes many types of hypervalent compounds, both thermodynamically and kinetically.[9] Utilizing the Martin ligand, we succeeded in isolating enantiomeric pairs of optically active 10-P-5 hydrophosphoranes **1**-S_P and **1**-R_P, thus indicating that the stereomutation between **1**-S_P and **1**-R_P was sufficiently frozen to permit isolation at room temperature (Scheme 1).[10] Furthermore, we

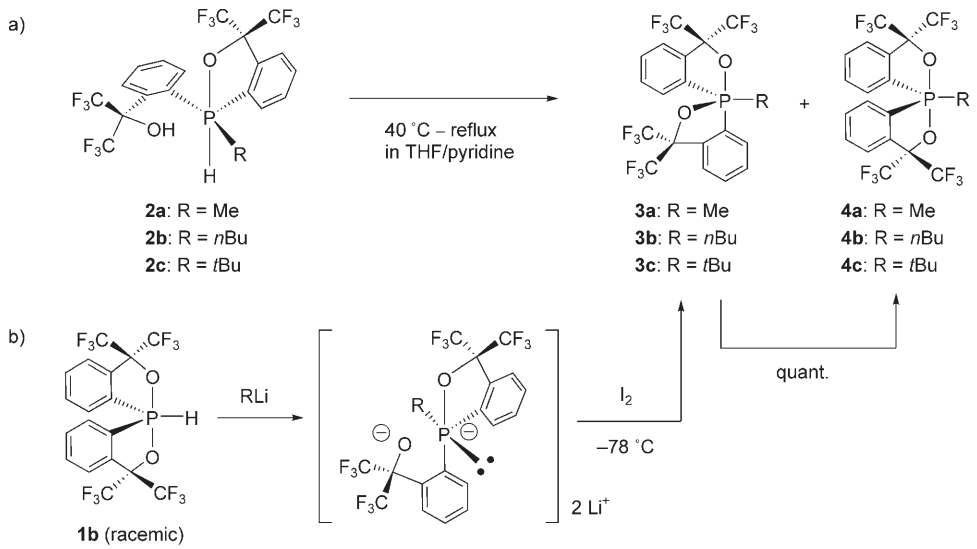


Scheme 1. Isolated enantiomeric pairs of optically active spirophosphoranes bearing Martin ligands.

isolated phosphoranes with an apical-oxygen-equatorial-carbon array (**3**; O-equatorial) as the major product by a thermal cyclization reaction of monocyclic P–H_{apical} phosphoranes **2** (Scheme 2a). This is the first isolated example of a phosphorane that violates the apicophilicity concept and can still be converted into its more-stable stereoisomer **4**, with two oxygen atoms at the apical sites (O-apical).[11] However, this method usually provides a mixture of **3** and **4**, and is therefore not the best way to prepare O-equatorial phosphoranes **3**, which may undergo stereomutation at these temperatures. We later found that the O-equatorial phosphoranes were exclusively prepared at lower-than-ambient temperature by oxidative cyclization of the dianionic phosphoranes with I_2 (Scheme 2b).[12] O-equatorial phosphoranes with a bulky aryl group (2,4,6-triisopropylphenyl) were also isolated by the same method. These O-equatorial phosphoranes isomerized irreversibly to their stable stereoisomers (O-apical) at elevated temperatures, indicating that the O-equatorial isomers are kinetic products. There are several examples of isolated phosphoranes exhibiting "reversed apicophilicity".[4i–k,13,14] Notably, by introducing very bulky bidentate ligands, some of these phosphoranes became thermodynamically stable species even though the regular configurations were allowed, and a new insight into apicophilicity was unveiled from the unique system.[4i–k,14]

Successful isolation of several pairs of O-equatorial and O-apical phosphoranes led us to investigate the difference in structure and reactivity of these stereoisomers. We found that O-equatorial phosphoranes **3** easily reacted with nucleophiles, whereas the O-apical isomers **4** did not react at all under similar conditions, and that the α-carbanion **5** derived from the O-equatorial isomer (Figure 1) was stablized by $n_C \rightarrow \sigma^*_{P-O}$ interactions; this finding was supported by theoretical calculations.[15] Moreover, O-equatorial phosphoranes **7** bearing a primary amine group were also isolated, and the energy of the $n_N \rightarrow \sigma^*_{P-O}$ interaction was quantitatively estimated to be about 4 kcal mol^{-1} based on kinetic measurements and theoretical calculations.[16]

As shown above, we succeeded in clarifying the property differences between isomeric phosphoranes, of which BPR was efficiently frozen by the use of the Martin ligand. However, we have not been successful in isolating phosphoranes that bear small or electronegative substituents as the equatorial monodentate ligand. For example, the stereomutation of O-equatorial methylphosphorane (**3a**) to the O-apical isomer **4a** was relatively fast even at room temperature; therefore, **3a** could not be isolated in pure form. In other words, to isolate a phosphorane with a small or electronegative group at the equatorial site, a bidentate ligand that suppresses BPR more efficiently than the Martin ligand is needed.



	Formation ratio		
Method	3a/4a	3b/4b	3c/4c
a	53 : 47	71 : 29	>99 : <1
b	>99 : <1	>99 : <1	>99 : <1

Scheme 2. Preparation of O-equatorial spirophosphoranes **3** and O-apical isomers **4** by a) dehydrogenative cyclization and b) oxidation of dianionic phosphorane.

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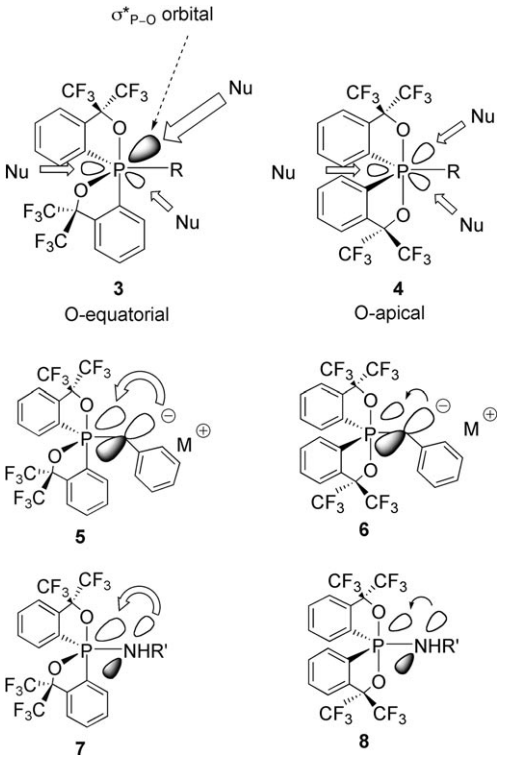


Figure 1. Enhanced electrophilicity of O-equatorial phosphorane **3** and the increased stability of the carbanion **5** and aminophosphorane **7** originating from the low-lying σ^*_{P-O} orbitals in the equatorial plane.

Herein, we present the synthesis of a new bidentate ligand bearing two pentafluoroethyl (C_2F_5) groups that is bulkier than the Martin ligand (Figure 2). The key reaction

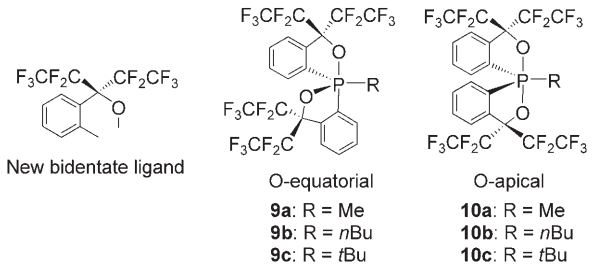


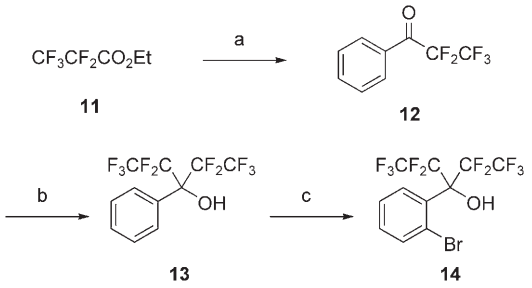
Figure 2. Spirophosphoranes that bear the new bidentate ligand.

of the synthesis is a Cannizzaro-type disproportionation involving intermolecular migration of the pentafluoroethyl group. The synthesis and structures of O-equatorial phosphoranes **9** bearing the bidentate ligands are then discussed. The crystal structures of **9** were found to be slightly different from those of the phosphoranes with Martin ligands **3**. A kinetic study of the stereomutation of the methyl derivative (**9a**→**10a**) revealed that the steric bulkiness of the C_2F_5 group actually raised the energy barrier to pseudorotation. Full details are shown herein.

Results and Discussion

Synthesis of 1,1,1,2,2,4,4,5,5,5-Decafluoro-3-phenyl-3-pentanol (13) by Cannizzaro-type Reaction and Ligand Precursor 14

Recently, two different methods for the synthesis of alcohol **13** by utilizing C_2F_5I were reported.[17] In these methods, however, the boiling point of C_2F_5I is so low (12–13 °C) that experimental operation becomes troublesome. Therefore, we exploited a new synthetic method for obtaining **13** and found that the Cannizzaro-type reaction[18] was convenient. At first, pentafluoropropiophenone (**12**) was prepared from ethyl pentafluoropropionate (**11**) with PhLi in 84% yield (Scheme 3). As reported previously, trifluoroacetophenone



Scheme 3. Synthesis of **13** and **14**. Reagents, conditions, and yields: a) PhLi (1.1 equiv), THF, −78 °C, 2 h, then 2 M HCl, 84%; b) *t*BuOK (0.5 equiv), THF, room temperature, 15 h, then CF_3COOH, CH_2Cl_2, 33%; c) *n*BuLi/TMEDA (3.0 equiv/3.0 equiv), hexane, room temperature, 36 h, then $BrCF_2CF_2Br$ (4.5 equiv), room temperature, 3 h, 84%.

functions as a trifluoromethyl anion source in the presence of *t*BuOK.[19] Therefore, we examined the use of this methodology for the synthesis of **13**. As expected, treatment of **12** with 0.5 equivalents of *t*BuOK in THF furnished the desired alcohol **13** in 33% yield (66% based on the C_2F_5 group). The reaction proceeded cleanly at room temperature, and the by-product, *tert*-butyl benzoate, was easily removed from **13** by treatment with trifluoroacetic acid. To our knowledge, this is the first example of a Cannizzaro-type disproportionation of a perfluoroalkyl group.

For the Martin ligand, it is known that hexafluorocumyl alcohol can be quantitatively dilithiated with a stoichiometric amount of *n*BuLi in the presence of a catalytic amount of *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA).[20] However, in the present case, dilithiation of **13** was not completed (up to 70%) by the same method. We found that 3 equivalents of *n*BuLi/TMEDA were needed for complete dilithiation of **13**. Therefore, **13** was converted into *o*-bromo derivative **14** in 84% yield, which was used as the precursor of the bidentate ligand (Scheme 3).

Dimetallation of 14 and Synthesis of P−H Spirophosphorane 16

At first, dimetallation of **14** was examined (Scheme 4). Compound **14** was treated with 2.2 equivalents of *n*BuLi followed

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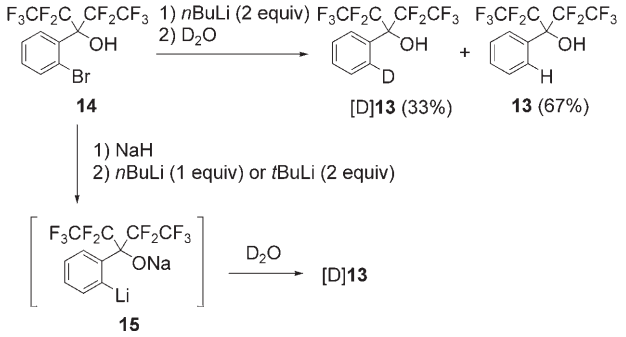
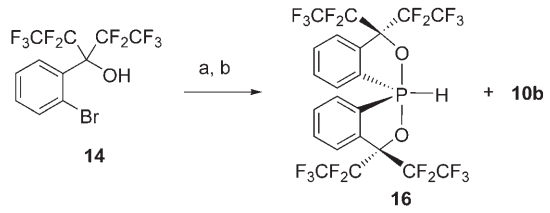


Scheme 4. Examination of the dimetallation of **14**.

by D_2O; partially deuterated **13** was produced ([D]**13**/**13** = 33:67). From this result, the lithium–bromine exchange reaction with *n*BuLi is clearly faster than abstraction of the hydroxy proton. Thus, the resulting aryllithium generated from the reaction of *n*BuLi with **14** was readily quenched by intramolecular proton transfer from the alcohol functionality. To avoid the intramolecular proton transfer, the combined system, NaH followed by *n*BuLi (or *t*BuLi), was employed. Based on the ^{1}H NMR spectrum, the bromine atom was found to be completely replaced with deuterium. This condition should be good in view of the reactivity of the dianion **15** and should be suitable for large-scale synthesis.

Dianion **15**, completely generated from **14** with the combined system of NaH and *n*BuLi as described above, was added to a solution of PCl_3 in THF to give P–H spirophosphorane **16** (50%) along with O-apical *n*-butylphosphorane (**10b**; 6%) (Scheme 5). The latter was provided by the reaction of the intermediate phosphoranide anion with *n*BuBr, which was formed during the dimetallation process. This problem was easily solved by the use of *t*BuLi instead of *n*BuLi, thus giving only **16** in 35% yield. The structure of **16** was confirmed by X-ray analysis and was found to be a TBP structure (Figure 3 and Table 1). The C1–P1–C2 angle of **16** (136.3°) in the equatorial plane was larger by 8.7° than that of P–H spirophosphorane **1b** (127.6°),[21] which bears Martin ligands. This is probably due to the steric repulsion between the bulky *endo*-C_2F_5 groups and the aromatic rings.



Scheme 5. Synthesis of hydrophosphorane **16**. Reagents, conditions, and yields: a) NaH (2.0 equiv), 0 °C, 0.5 h, THF, then *n*BuLi (1.0 equiv), −78 °C, 1 h, room temperature, 1 h; b) PCl_3 (0.5 equiv), −78 °C, 0.5 h, 0 °C, 1.5 h, then 6 M HCl, **16**: 50%, **10b**: 6%.

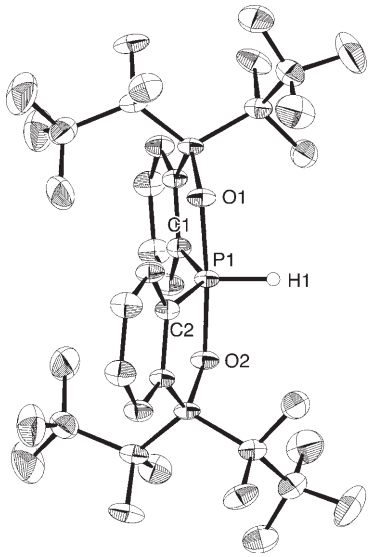
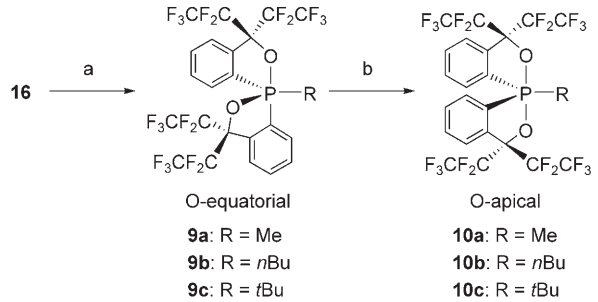


Figure 3. ORTEP diagram of hydrophosphorane **16** with the thermal ellipsoids shown at the 30% probability level. All hydrogen atoms other than H1 are omitted for clarity. Selected bond lengths (Å) and angles (°): P1–O1 1.736(3), P1–O2 1.736(3), P1–C1 1.823(4), P1–C2 1.823(4), P1–H1 1.330(7); O1–P1–O2 175.00(3), O1–P1–C1 90.33(17), O1–P1–C2 87.79(16), O1–P1–H1 92.52(14), O2–P1–C1 87.79(16), O2–P1–C2 90.33(17), O2–P1–H1 92.52(14), C1–P1–C2 136.30(3), C1–P1–H1 111.85(16), C2–P1–H1 111.85(16).

Synthesis of O-Equatorial Spirophosphoranes 9

The O-equatorial phosphoranes **9a–c** were prepared from the reaction of P–H phosphorane **16** with 3 equivalents of RLi followed by treatment with I_2.[12] All the O-equatorial phosphoranes were almost quantitatively converted into the corresponding O-apical phosphoranes by heating in solution (Scheme 6). Notably, the O-equatorial isomer was isolated in pure form in the case of the methyl derivative **9a**. This clearly indicates that stereomutation of **9a** to **10a** is sufficiently suppressed to permit isolation. The ^{31}P NMR signals for the O-equatorial isomer (δ = −4.7 (**9a**), −1.5 (**9b**), and 11.2 ppm (**9c**) in $CDCl_3$) are shifted downfield compared to those of the O-apical isomer (δ = −21.2 (**10a**), −16.1 (**10b**),



Scheme 6. Synthesis of O-equatorial spirophosphoranes **9** and isomerization of **9** to **10**. Reagents, conditions, and yields: a) RLi (3.0 equiv), Et_2O, room temperature, 3 h, then I_2 (3.0 equiv), −78 °C to room temperature, 3 h, **9a**: 90%, **9b**: 92%, **9c**: 43%; b) **10a**: C_6D_6, 75 °C, 8 h, 98%; **10b**: C_6D_6, 80 °C, 12 h, 100%; **10c**: diglyme, 195 °C, 3 weeks, 92%.

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Table 1. Crystallographic data for **16**, **9a–c**, **10a**, and **10b**.

Compound	**16**	**9a**	**9b**	**9c**	**10a**	**10b**
Formula	$C_{22}H_9F_{20}O_2P$	$C_{23}H_{11}F_{20}O_2P$	$C_{26}H_{17}F_{20}O_2P$	$C_{26}H_{17}F_{20}O_2P$	$C_{23}H_{11}F_{20}O_2P$	$C_{26}H_{17}F_{20}O_2P$
M_r	716.26	730.29	772.37	772.37	730.29	772.37
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic	orthorhombic	triclinic
Space group	$C2/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$	$Pbcn$	$P\bar{1}$
Color	colorless	colorless	colorless	colorless	colorless	colorless
Habit	plate	plate	plate	plate	plate	plate
Crystal dimensions [mm]	0.60×0.60×0.60	0.40×0.40×0.40	0.50×0.20×0.20	0.50×0.40×0.40	0.50×0.20×0.20	0.90×0.70×0.50
a [Å]	9.2910(3)	11.5700(2)	8.8950(2)	12.6860(2)	18.7160(5)	9.678(3)
b [Å]	14.4960(5)	13.6760(3)	19.7730(4)	12.9690(2)	8.3700(10)	10.044(6)
c [Å]	19.3220(8)	16.8200(4)	17.1150(5)	18.6730(4)	17.0800(4)	16.385(5)
α [°]	90	90	90	90	90	103.63(4)
β [°]	102.2320(10)	98.4340(10)	103.1120(10)	109.0380(10)	90	95.28(2)
γ [°]	90	90	90	90	90	101.18(4)
V [Å^3]	2543.25(16)	2632.67(10)	2931.72(12)	2904.13(9)	2675.63(10)	1502.6(11)
Z	4	4	4	4	4	2
D_{calcd} [g cm^{-3}]	1.871	1.842	1.750	1.767	1.813	1.707
Abs. coeff. [mm^{-1}]	0.277	0.270	0.248	0.250	0.266	0.242
$F(000)$	1408	1440	1536	1536	1440	768
Radiation, λ [Å]	$Mo_{K\alpha}$, 0.71073	$Mo_{K\alpha}$, 0.71073	$Mo_{K\alpha}$, 0.71073	$Mo_{K\alpha}$, 0.71073	$Mo_{K\alpha}$, 0.71073	$Mo_{K\alpha}$, 0.71073
T [K]	298(2)	298(2)	298(2)	298(2)	298(2)	298(2)
Data collcted	$+h, +k, \pm l$	$+h, +k, \pm l$	$+h, +k, \pm l$	$+h, +k, \pm l$	$+h, +k, +l$	$\pm h, -k, \pm l$
Data/restrains/parameters	2594/0/206	5958/0/416	6519/0/479	6965/0/537	3169/0/210	5251/0/503
R_1 ($I>2\sigma(I)$)	0.0737	0.0649	0.0758	0.0688	0.0580	0.0927
wR_2 (all data)	0.2470	0.2034	0.2541	0.2089	0.1750	0.3155
GOF	1.197	1.074	1.095	1.055	1.123	1.471
Solvent for crystallization	*n*-hexane/Et_2O	CH_3CN	CH_3CN	$CHCl_3$	$CHCl_3$	$CHCl_3$

and −3.2 ppm (**10c**) in $CDCl_3$), and are the same as those for the CF_3 derivatives **3** and **4**.[11b]

The structures of **9a–c**, **10a**, and **10b** were confirmed by X-ray analysis (Figure 4 and Tables 1 and 2), which show that all the structures have slightly distorted TBP geometry.[22] We found that the steric bulk of the pentafluoroethyl groups slightly affected the crystal structures by comparing CF_3 derivatives **3b** and **4b** with the C_2F_5 derivatives **9b** and **10b** (Figure 5 and Table 2). For the O-apical **4b** and **10b**, the apical P–O distances (1.763(1) and 1.754(1) Å for **4b**, 1.759(3) and 1.750(3) Å for **10b**) were very similar, and the C1–P1–C2 angle of **10b** (134.28°) is expanded by 7.3° compared to that of **4b** (127.0°). This is due to steric repulsion between the *endo*-C_2F_5 group and the equatorial aromatic ring. On the other hand, in the O-equatorial **3b**[11a] and **9b**, the apical P1–O1 bond of **9b** (1.800(2) Å) is longer than the corresponding bond of **3b** (1.770(3) Å) by 0.03 Å. Because CF_3 groups are small, steric hindrance in **3b** is negligible. However, steric repulsion between the *endo*-C_2F_5 groups of **9b** is inevitable; therefore, the apical P1–O1 bond of **9b** is forced to become somewhat more elongated than that of **3b**. Other structural parameters obtained for **3b** and **9b** around the phosphorus atom were very similar.

Kinetic Study of the Isomerization of O-equatorial 9a to O-apical 10a

The successful isolation of **9a** shows its high stability at room temperature; therefore, we discuss further the stereomutation of **9a** on the basis of a kinetic study. Figure 6 shows a representative example of the stereomutation monitored by ^{1}H NMR spectroscopy. The rate of isomerization of **9a** to **10a** was measured in C_6D_6 in the temperature range 323–343 K by monitoring the change in the integrals of the ^{1}H NMR signals of the methyl group. The isomerization proceeded with first-order kinetics. The activation parameters obtained from the Eyring plot are as follows: $\Delta S^{\neq} = (-5.1 \pm 2.4)$ e.u., $\Delta H^{\neq} = (24.4 \pm 0.8)$ kcal mol^{-1}, $\Delta G^{\neq}_{333} = 26.1$ kcal mol^{-1} (Figure 7 and Table 3). The activation free energy for the steromutation of **9a** to **10a** was actually higher than that of **3a** to **4a** ($\Delta G^{\neq}_{333} = 22.5$ kcal mol^{-1})[16] by 3.6 kcal mol^{-1}, indicating that the steric effect of the C_2F_5 group was more effective for freezing pseudorotation than that of the CF_3 group.

As previously proposed by our group,[11] isomer **17a**, which bears one of the two bidentate ligands at the diequatorial sites, would be the isomer highest in energy; therefore, the structure of this isomer is assumed to be similar to that of the actual transition state (TS) for the stereomutation (Figure 8). The difference in the activation enthalpy ($\Delta H^{\neq} =$ 19.3 kcal mol^{-1} for **3a** to **4a**,[16] 24.4 kcal mol^{-1} for **9a** to **10a**) contributes mainly to the difference in the activation free energy. This could mean that the steric repulsion between the Rf group and the aromatic ring of the diequatorial bidentate ligand in **18a** (Rf = C_2F_5) is larger than that of **17a** (Rf = CF_3), thus causing the new bidentate ligand with C_2F_5 groups to be more effective in freezing pseudorotation than the Martin ligand.

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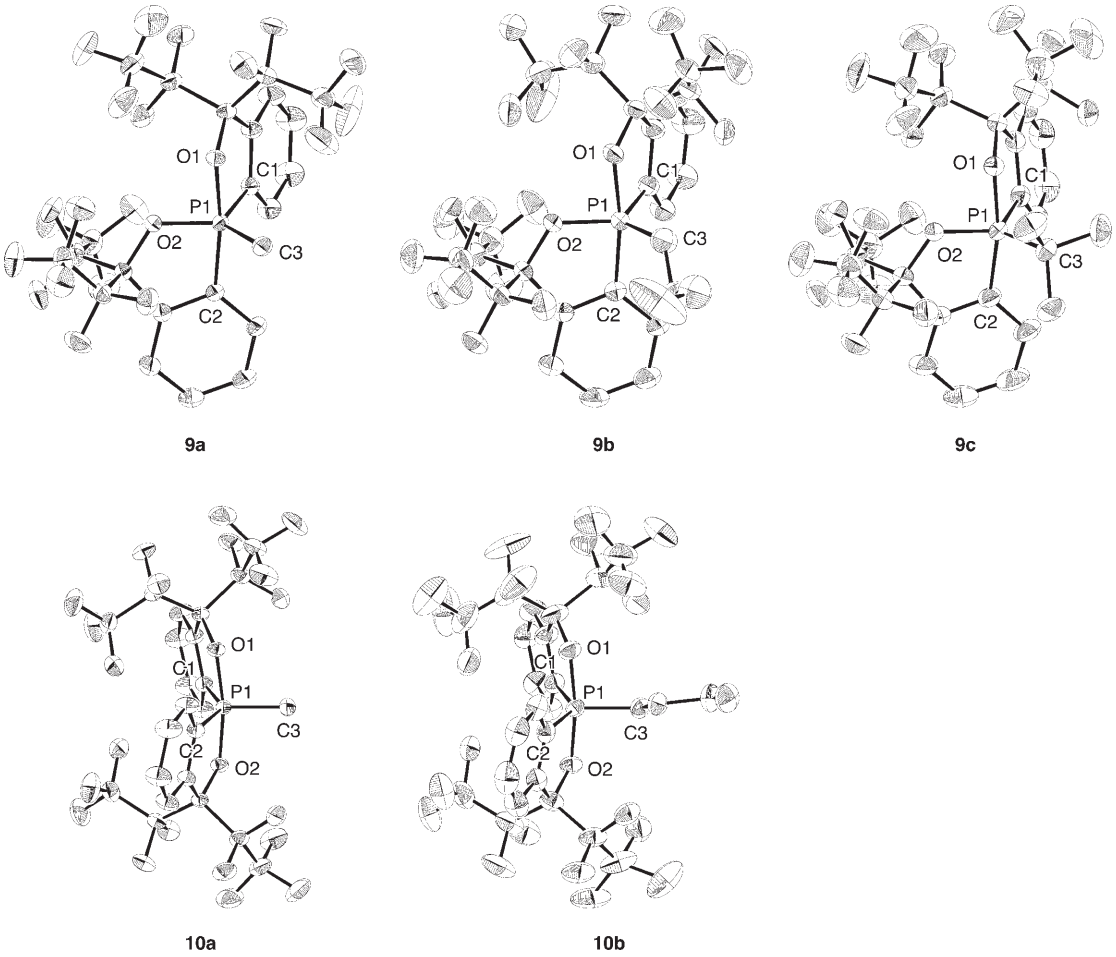

Figure 4. ORTEP diagram of phosphoranes **9a–c**, **10a**, and **10b** with the thermal ellipsoids shown at the 30% probability level. All hydrogen atoms are omitted for clarity.

Table 2. Selected bond lengths [Å] and angles [°] for **9a–c**, **10a**, **10b**, **3b**,[11a] and **4b**.[11a]

	9a	**9b**	**9c**	**10a**	**10b**	**3b**[11a]	**4b**[11a]
P1–O1	1.7858(17)	1.800(2)	1.8031(15)	1.7588(12)	1.759(3)	1.770(3)	1.763(1)
P1–O2	1.6547(17)	1.661(2)	1.6639(15)	1.7588(12)	1.750(3)	1.660(3)	1.754(1)
P1–C1	1.827(2)	1.828(3)	1.837(2)	1.8320(17)	1.829(4)	1.810(4)	1.816(1)
P1–C2	1.879(2)	1.864(3)	1.886(2)	1.8320(17)	1.824(4)	1.866(4)	1.817(1)
P1–C3	1.814(3)	1.841(4)	1.902(2)	1.810(3)	1.826(4)	1.832(5)	1.818(1)
O1–P1–O2	83.89(8)	83.27(9)	82.94(7)	169.32(9)	170.95(13)	82.8(2)	175.8(1)
O1–P1–C1	86.38(9)	86.11(11)	85.21(8)	89.29(7)	86.62(15)	87.4(2)	87.3(1)
O1–P1–C2	171.58(10)	170.97(12)	169.76(9)	86.80(7)	90.16(16)	170.5(2)	90.6(1)
O1–P1–C3	88.55(11)	88.94(17)	88.90(9)	95.34(5)	93.37(16)	88.7(2)	91.2(1)
O2–P1–C1	119.52(10)	119.67(13)	118.02(9)	86.80(7)	89.49(14)	120.1(2)	91.0(1)
O2–P1–C2	87.92(9)	87.70(12)	87.21(9)	89.29(7)	86.71(15)	87.8(2)	87.3(1)
O2–P1–C3	117.97(11)	117.58(19)	119.06(10)	95.34(5)	95.67(15)	124.1(2)	93.0(1)
C1–P1–C2	99.42(11)	98.46(13)	97.02(10)	137.10(12)	134.28(16)	98.8(2)	127.0(1)
C1–P1–C3	121.27(12)	121.4(2)	121.26(11)	111.45(6)	112.73(17)	114.5(2)	116.5(1)
C2–P1–C3	93.57(12)	95.23(18)	98.37(11)	111.45(6)	112.98(16)	95.2(2)	116.5(1)

Conclusions

1,1,1,2,2,4,4,5,5,5-Decafluoro-3-phenyl-3-pentanol (**13**) was synthesized by a Cannizzaro-type reaction in 28% overall yield. During the examination of the dimetallation of **14**, it was found that the lithium–bromine exchange reaction was faster than abstraction of the hydroxy proton with the use of *n*BuLi. This problem was easily resolved by using the combined system, NaH followed by *n*BuLi (or *t*BuLi). With the dianion **15**, P–H spirophosphorane **16** was obtained in a

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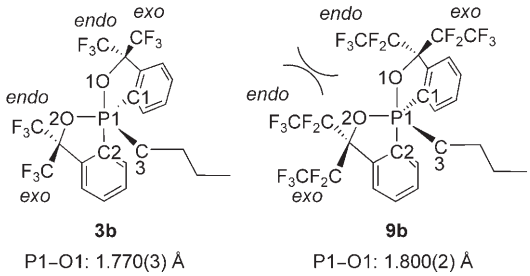

Figure 5. Steric repulsion of *endo*-C_2F_5 groups in the crystal structure of **9b**.

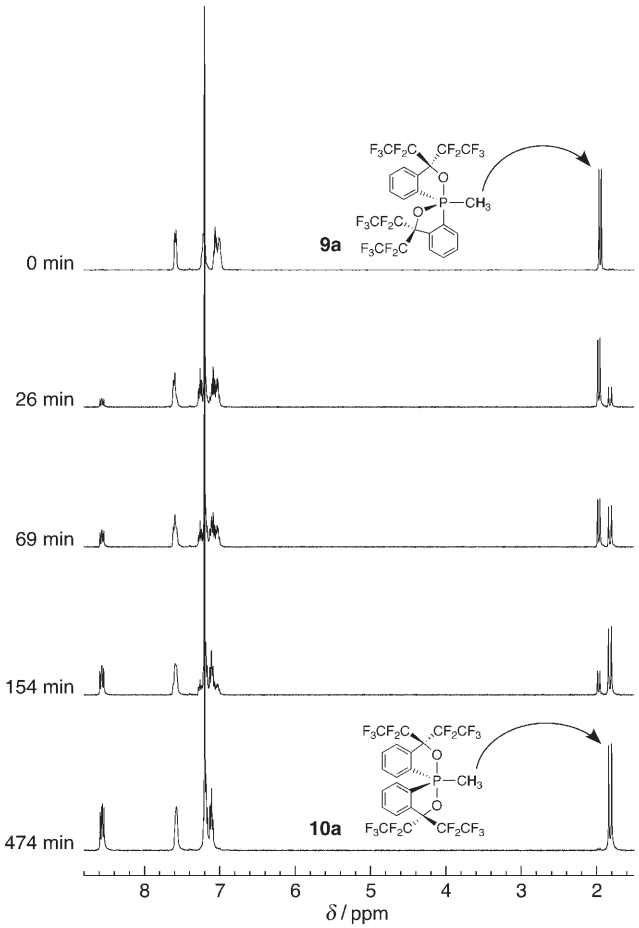

Figure 6. Time course of the ^{1}H NMR signals of the isomerization of **9a** to **10a** in C_6D_6 at 70 °C.

moderate yield of 50%. The O-equatorial phosphoranes **9** were synthesized and successfully isolated. According to X-ray analysis, steric repulsion between the *endo*-C_2F_5 groups slightly affected the structure and forced the apical P1–O1 bond to elongate in **9b** relative to CF_3 derivative **3b**. The kinetic study revealed that the steric hindrance of the C_2F_5 group was more effective for freezing pseudorotation than that of the CF_3 group. Further synthetic studies of hypervalent compounds with the new bidentate ligand are ongoing.

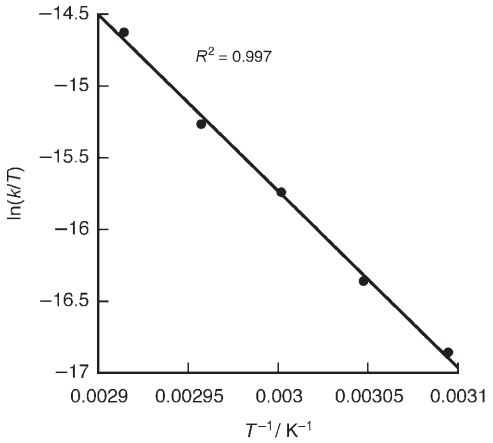

Figure 7. Eyring plot for the isomerization of **9a** to **10a**.

Table 3. Rate constants and activation parameters for stereomutation from **9a** to **10a**.

T [K]	k[a] [s^{-1}]	$\Delta G^{\neq}$ [kcal mol^{-1}]	$\Delta H^{\neq}$ [kcal mol^{-1}]	$\Delta S^{\neq}$ [e.u.]
323	$(1.51\pm0.01)\times10^{-5}$	26.00		
328	$(2.55\pm0.02)\times10^{-5}$	26.03		
333	$(4.76\pm0.03)\times10^{-5}$	26.06	24.4 ± 0.8	-5.1 ± 2.4
338	$(7.70\pm0.06)\times10^{-5}$	26.08		
343	$(15.0\pm0.18)\times10^{-5}$	26.11		

[a] Error is given as the standard deviation.

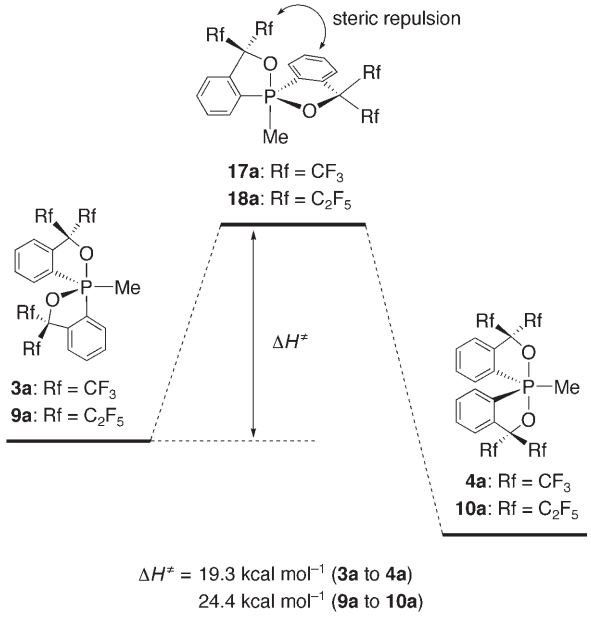

Figure 8. Energy-level diagram for the isomerization of O-equatorial phosphorane to the O-apical isomer.

Experimental Section

General

Melting points were measured with a Yanaco micro-melting-point apparatus. ^{1}H NMR (400 MHz), ^{19}F NMR (376 MHz), and ^{31}P NMR

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(162 MHz) spectra were recorded on a JEOL EX-400 or a JEOL AL-400 spectrometer. ^{1}H NMR chemical shifts (δ) are given in ppm downfield from Me_4Si, determined by residual chloroform ($\delta = 7.26$ ppm). ^{19}F NMR chemical shifts are given in ppm downfield from external $CFCl_3$. ^{31}P NMR chemical shifts are given in ppm downfield from external 85% H_3PO_4. Elemental analysis was performed with 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 other solvents were distilled over CaH_2. Merck silica gel 60 was used for column chromatography.

Syntheses

12: Under N_2, PhLi (in 1.05 M cyclohexane/Et_2O, 100 mL, 105 mmol) was added to a solution of **7** (17.9 g, 93.4 mmol) in THF (224 mL) at −78 °C, and the mixture was stirred for 2 h at the same temperature. The reaction mixture was then treated with HCl (2 M, 60 mL) at −78 °C and stirred for 10 h at room temperature. The mixture was extracted with Et_2O (2× 150 mL), and the organic layer was washed with brine (2×80 mL) and dried over anhydrous $MgSO_4$. After the solvents were removed by evaporation, the yellow oil was subjected to distillation to afford **12** (17.6 g, 78.7 mmol, 84%) as a colorless liquid. B.p.: 61.2–62.0 °C (26 mmHg; reference [17a]: 76–78 °C at 29 mmHg); ^{1}H NMR ($CDCl_3$): $\delta = 8.09$ (d, $^3J_{H-H} = 8$ Hz, 2H), 7.72 (t, $^3J_{H-H} = 8$ Hz, 1H), 7.55 ppm (t, $^3J_{H-H} = 8$ Hz, 2H); ^{19}F NMR ($CDCl_3$): $\delta = -82.0$ (s, 3F), −116.0 ppm (s, 2F).

13: Under N_2, *t*BuOK (in 1.0 M THF, 12.5 mL, 12.5 mmol) was added to a solution of **12** (5.51 g, 24.6 mmol) in THF (50 mL) at 0 °C, and the mixture was stirred for 15 h at room temperature. After the solvent was removed by evaporation, CH_2Cl_2 (5.6 mL) was added. Trifluoroacetic acid (7.5 mL, 101 mmol) was added to the mixture at 0 °C, and the mixture was stirred for 60 h at room temperature. The reaction was quenched with saturated aqueous Na_2CO_3 (80 mL). The mixture was extracted with Et_2O (2×100 mL), and the organic layer was washed with brine (2× 50 mL) and dried over anhydrous $MgSO_4$. After solvent removal by evaporation, the yellow oil was separated by column chromatography (CH_2Cl_2/*n*-hexane/benzene = 1:6:0.21) followed by distillation to afford **13** (2.86 g, 8.30 mmol, 33%) as a colorless liquid. B.p.: 35.0–36.0 °C (0.7 mmHg; reference [17a]: 55–56 °C at 4 mmHg); ^{1}H NMR ($CDCl_3$): $\delta = 7.72$ (d, $^3J_{H-H} = 7.6$ Hz, 2H), 7.42–7.47 (m, 3H), 3.57 ppm (brs, 1H); ^{19}F NMR ($CDCl_3$): $\delta = -78.4$ (s, 6F), −120.3 ppm (s, 4F); MS (FAB): $m/z = 344$ $[M]^+$, 327 $[M-OH]^+$, 225 $[M-C_2F_5]^+$.

14: Under Ar, TMEDA (2.20 mL, 14.6 mmol) was added to *n*BuLi (in 1.59 M *n*-hexane, 9.20 mL, 14.6 mmol) at room temperature, and the mixture was stirred for 30 min. Compound **13** (1.68 g, 4.88 mmol) was then added at 0 °C, and the mixture was stirred for 36 h at room temperature. 1,2-Dibromo-1,1,2,2-tetrafluoroethane (2.60 mL, 21.8 mmol) was added at −78 °C, and the mixture was stirred for 3 h at room temperature. The reaction was quenched with HCl (2 M, 40 mL) at 0 °C. The mixture was extracted with Et_2O (2×50 mL), and the organic layer was washed with brine (2×30 mL) and dried over anhydrous $MgSO_4$. After solvent removal by evaporation, the yellow oil was separated by column chromatography (CH_2Cl_2/*n*-hexane/benzene = 1:6:0.21) followed by distillation to afford **14** (1.73 g, 4.09 mmol, 84%) as a colorless liquid. B.p.: 66.0–67.0 °C (0.7 mmHg); ^{1}H NMR ($CDCl_3$): $\delta = 7.75$ (brd, $^3J_{H-H} = 8$ Hz, 1H), 7.69 (dd, $^3J_{H-H} = 8$ Hz, $^4J_{H-H} = 1$ Hz, 1H), 7.41 (td, $^3J_{H-H} = 8$ Hz, $^4J_{H-H} = 1$ Hz, 1H), 7.33 (td, $^3J_{H-H} = 8$ Hz, $^4J_{H-H} = 1$ Hz, 1H), 5.50 ppm (brs, 1H); ^{19}F NMR ($CDCl_3$): $\delta = -78.1$ (m, 6F), −116.6 (d, $^2J_{F-F} = 290$ Hz, 2F), −117.7 ppm (d, $^2J_{F-F} = 290$ Hz, 2F) .

16: Under N_2, a solution of **14** (563 mg, 1.33 mmol) in THF (4 mL) was added to a suspension of NaH (106 mg, 2.65 mmol) in THF (2 mL) at 0 °C, and the mixture was stirred for 0.5 h at room temperature. The mixture was then cooled at −78 °C, *n*BuLi (in 1.59 M *n*-hexane, 0.84 mL, 1.33 mmol) was added, and the mixture was stirred for 1 h at the same temperature. After that, the mixture was transferred to a solution of PCl_3 (0.058 mL, 0.663 mmol) in THF (4 mL) at −78 °C and stirred for 0.5 h. The mixture was warmed to 0 °C and stirred for 1.5 h. The reaction was quenched with HCl (6 M, 10 mL) at 0 °C. The mixture was extracted with diethyl ether (2×50 mL), and the organic layer was washed with brine (2×40 mL) and dried over anhydrous $MgSO_4$. After solvent removal by evaporation, the resulting crude product was separated by column chromatography (*n*-hexane) to afford **16** (238 mg, 0.333 mmol, 50%) and **10b** (30.7 mg, 0.039 mmol, 6%) as white solids. Colorless crystals of **16** and **10b** suitable for X-ray analysis were obtained by recrystallization from *n*-hexane/diethyl ether and $CHCl_3$, respectively. **16**: M.p.: 135.0–136.0 °C; ^{1}H NMR ($CDCl_3$): $\delta = 8.41$–8.36 (m, 2H), 7.96 (d, $^1J_{H-P} = 703$ Hz, 1H), 7.81–7.72 ppm (m, 6H); ^{19}F NMR ($CDCl_3$): $\delta = -78.2$ (s, 6F), −79.9 (dd, $^3J_{F-F} = 12$, 4 Hz, 6F), −116.5 (dq, $^2J_{F-F} = 288$ Hz, $^3J_{F-F} = 4$ Hz, 2F), −117.6 (d, $^2J_{F-F} = 288$ Hz, 2F), −118.5 (d, $^2J_{F-F} = 288$ Hz, 2F), −120.6 ppm (dq, $^2J_{F-F} = 288$ Hz, $^3J_{F-F} = 12$ Hz, 2F); ^{31}P NMR ($CDCl_3$): $\delta = -47.2$ ppm; elemental analysis: calcd (%) for $C_{22}H_9F_{20}O_2P$: C 36.89, H 1.27; found: C 36.95, H 1.56. **10b**: M.p.: 101.0–102.0 °C; ^{1}H NMR ($CDCl_3$): $\delta = 8.47$–8.41 (m, 2H), 7.75–7.66 (m, 6H), 2.19–2.00 (m, 2H), 1.15–1.26 (m, 4H), 0.75 ppm (t, $^3J_{H-H} = 8$ Hz, 3H); ^{19}F NMR ($CDCl_3$): $\delta = -78.5$ (s, 6F), −79.5 (d, $^3J_{F-F} = 19$ Hz, 3F), −79.6 (d, $^3J_{F-F} = 19$ Hz, 3F), −116.3 (dd, $^2J_{F-F} = 290$ Hz, $^4J_{F-F} = 35$ Hz, 2F), −116.4 (dq, $^2J_{F-F} = 290$ Hz, $^3J_{F-F} = 19$ Hz, 2F), −117.4 (d, $^2J_{F-F} = 290$ Hz, 2F), −121.1 ppm (dd, $^2J_{F-F} = 290$ Hz, $^4J_{F-F} = 35$ Hz, 2F); ^{31}P NMR ($CDCl_3$): $\delta = -16.1$ ppm; elemental analysis: calcd (%) for $C_{26}H_{17}F_{20}O_2P$: C 40.43, H 2.22; found: C 40.72, H 2.39.

9a: Under Ar, MeLi (in 0.92 M diethyl ether, 0.45 mL, 0.414 mmol) was added to a solution of **16** (104 mg, 0.145 mmol) in Et_2O (4.5 mL) at 0 °C. The mixture was then stirred for 3 h at room temperature. I_2 (110 mg, 0.439 mmol) was added at −78 °C, and the mixture was stirred for 3 h at room temperature. The reaction was quenched with aqueous $Na_2S_2O_3$ (20 mL). The mixture was extracted with Et_2O (2×50 mL), and the organic layer was washed with brine (2×50 mL) and dried over anhydrous $MgSO_4$. After solvent removal by evaporation, the resulting crude product was separated by column chromatography (CH_2Cl_2/*n*-hexane = 1:2) to afford **9a** (96 mg, 0.131 mmol, 90%) as a white solid. Colorless crystals of **9a** suitable for X-ray analysis were obtained by recrystallization from CH_3CN. M.p.: 99.5–100.4 °C (decomp.); ^{1}H NMR ($CDCl_3$): $\delta = 7.75$ (brs, 2H), 7.70–7.60 (m, 6H), 2.23 ppm (d, $^2J_{H-P} = 12$ Hz, 3H); ^{19}F NMR ($CDCl_3$): $\delta = -79.0$ (s, 12F), −115.9 (brs, 4F), −116.5 ppm (brs, 4F); ^{31}P NMR ($CDCl_3$): $\delta = -4.7$ ppm; elemental analysis: calcd (%) for $C_{23}H_{11}F_{20}O_2P$: C 37.83, H 1.52; found: C 37.81, H 1.71.

9b: Under Ar, *n*BuLi (in 1.59 M *n*-hexane, 0.120 mL, 0.190 mmol) was added to a solution of **16** (45 mg, 0.063 mmol) in Et_2O (1.3 mL) at 0 °C, and the mixture was then stirred for 3 h at room temperature. I_2 (49 mg, 0.19 mmol) was added at −78 °C, and the mixture was stirred for 3 h at room temperature. The reaction was quenched with aqueous $Na_2S_2O_3$ (15 mL). The mixture was extracted with Et_2O (2×40 mL), and the organic layer was washed with brine (2×30 mL) and dried over anhydrous $MgSO_4$. After solvent removal by evaporation, the resulting crude product was separated by column chromatography (CH_2Cl_2/*n*-hexane = 1:2) to afford **9b** (45 mg, 0.058 mmol, 92%) as a white solid. Colorless crystals of **9b** suitable for X-ray analysis were obtained by recrystallization from CH_3CN. M.p.: 71.0–72.0 °C (decomp.); ^{1}H NMR ($CDCl_3$): $\delta = 7.57$–7.62 (m, 4H), 7.73–7.79 (m, 4H), 2.43–2.35 (m, 2H), 1.58–1.51 (m, 2H), 1.32–1.20 (m, 2H), 0.80 ppm (t, $^3J_{H-H} = 8$ Hz, 3H); ^{19}F NMR ($CDCl_3$): $\delta = -79.1$ (brs, 12F), −116.0 (brs, 4F), −116.2 ppm (brs, 4F); ^{31}P NMR ($CDCl_3$): $\delta = -1.5$ ppm; elemental analysis: calcd (%) for $C_{26}H_{17}F_{20}O_2P$: C 40.43, H 2.22; found: C 40.68, H 2.37.

9c: Under Ar, *t*BuLi (in 1.50 M *n*-pentane, 0.22 mL, 0.330 mmol) was added to a solution of **16** (80.0 mg, 0.117 mmol) in Et_2O (3.0 mL) at 0 °C, and the mixture was then stirred for 3 h at room temperature. I_2 (82 mg, 0.32 mmol) was added at −78 °C, and the mixture was stirred for 3 h at room temperature. The reaction was quenched with aqueous $Na_2S_2O_3$ (20 mL). The mixture was extracted with Et_2O (2×40 mL), and the organic layer was washed with brine (2×30 mL) and dried over anhydrous $MgSO_4$. After solvent removal by evaporation, the resulting crude product was separated by column chromatography (CH_2Cl_2/*n*-hexane = 1:2) to afford **9c** (39 mg, 0.050 mmol, 43%) as a white solid. Colorless crystals of **9c** suitable for X-ray analysis were obtained by recrystallization from $CHCl_3$. M.p.: 138.0–139.0 °C; ^{1}H NMR ($CDCl_3$): $\delta = 8.01$ (dd, $^3J_{P-H} = 8$ Hz, $^3J_{H-H} = 8$ Hz, 2H), 7.72 (d, $^3J_{H-H} = 8$ Hz, 2H), 7.60–7.52 (m, 4H), 1.20 ppm (d, $^3J_{H-P} = 20$ Hz, 9H); ^{19}F NMR ($CDCl_3$): $\delta = -78.7$ (brs, 12F),

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−112.7 (d, $^2J_{F-F}$=293 Hz, 4F), −114.9 (d, $^2J_{F-F}$=293 Hz, 2F), −116.3 ppm (d, $^2J_{F-F}$=293 Hz, 2F); ^{31}P NMR ($CDCl_3$): δ=11.2 ppm; elemental analysis: calcd (%) for $C_{26}H_{17}F_{20}O_2P$: C 40.43, H 2.22; found: C 40.65, H 2.40.

10a: A solution of **9a** (30 mg, 0.041 mmol) in C_6D_6 (0.6 mL) was heated at 70 °C for 8 h. After concentration in vacuo, **10a** was obtained (29.3 mg, 0.0401 mmol, 98%) as a white solid. Colorless crystals of **10a** suitable for X-ray analysis were obtained by recrystallization from $CHCl_3$. M.p.: 108.0–108.8 °C; ^{1}H NMR ($CDCl_3$): δ=8.49–8.44 (m, 2H), 7.62–7.75 (m, 6H), 1.93 ppm (d, $^2J_{H-P}$=16 Hz, 3H); ^{19}F NMR ($CDCl_3$): δ=−78.4 (s, 6F), −79.6 (d, $^3J_{F-F}$=19.5 Hz, 6F), −115.6 (d, $^2J_{F-F}$=289 Hz, 2F), −116.2 (dq, $^2J_{F-F}$=289 Hz, $^3J_{F-F}$=19.5 Hz, 2F), −117.0 (dd, $^2J_{F-F}$=289 Hz, $^4J_{F-F}$=40.6 Hz, 2F), −121.0 ppm (dd, $^2J_{F-F}$=289 Hz, $^4J_{F-F}$=40.6 Hz, 2F); ^{31}P NMR ($CDCl_3$): δ=−21.2 ppm; elemental analysis: calcd (%) for $C_{23}H_{11}F_{20}O_2P$: C 37.83, H 1.52; found: C 37.64, H 1.39.

10b: A solution of **9b** (10.9 mg, 0.014 mmol) in C_6D_6 (0.5 mL) was heated at 80 °C for 12 h. After concentration in vacuo, **10b** was obtained (10.9 mg, 0.014 mmol, 100%) as a white solid. The spectral data were consistent with those of the same product obtained as the by-product in the synthesis of **16**.

10c: A solution of **9c** (13.2 mg, 0.017 mmol) in diglyme (0.5 mL) was heated at 195 °C for 3 weeks. The mixture was then extracted with Et_2O (2×10 mL), and the organic layer was washed with brine (2×10 mL) and dried over anhydrous $MgSO_4$. After concentration in vacuo, **10c** was obtained (12.2 mg, 0.015 mmol, 92%) as a white solid. M.p.: 116.3–117.0 °C; ^{1}H NMR ($CDCl_3$): δ=8.43–8.38 (m, 2H), 7.69 (brs, 2H), 7.61–7.65 (m, 4H), 1.04 ppm (d, $^3J_{H-P}$=20 Hz, 9H); ^{19}F NMR ($CDCl_3$): δ=−78.2 (d, $^3J_{F-F}$=21 Hz, 6F), −78.4 (d, $^3J_{F-F}$=21 Hz, 6F), −112.0 (d, $^2J_{F-F}$=296 Hz, 4F), −114.5 (d, $^2J_{F-F}$=296 Hz, 4F), −115.3 (dq, $^2J_{F-F}$=296 Hz, $^3J_{F-F}$= 21 Hz, 2F), −116.1 ppm (dq, $^2J_{F-F}$=296 Hz, $^3J_{F-F}$=21 Hz, 2F); ^{31}P NMR ($CDCl_3$): δ=−3.2 ppm.

Single-Crystal X-ray Analysis of 9a–c, 10a, 10b, and 16

For **10b**, crystals suitable for X-ray structural determination were mounted on a Mac Science MXC-κ diffractometer and irradiated with graphite-monochromated $Mo_{K\alpha}$ radiation (λ=0.71073 Å) for data collection. The lattice parameters were determined by a least-squares fitting of 31 reflections with $31<2\theta<35°$. Data were collected in the $2\theta/\omega$ scan mode. For **9a–c**, **10a**, and **16**, crystals suitable for X-ray structural determination were mounted on a Mac Science DIP2030 imaging plate diffractometer and irradiated with graphite-monochromated $Mo_{K\alpha}$ radition (λ= 0.71073 Å) for data collection. The unit-cell parameters were determined by separately autoindexing several images in each dataset with the DENZO program (MAC Science).[23] For each dataset, the rotation images were collected in 3° increments with a total rotation of 180° about the ϕ axis. The data were processed with SCALEPACK. The structures were solved by direct methods with the SHELX-97 program.[24] Refinement on F^2 was carried out with full-matrix least-squares by using the SHELX-97 program.[24] All non-hydrogen atoms were refined using anisotropic thermal parameters. The H1 atom of **16** was located by the differential Fourier synthesis. Hydrogen atoms were included in the refinement along with isotropic thermal parameters. The crystallographic data are summarized in Table 1.

CCDC-621574 (**9a**), -621575 (**9b**), -621576 (**9c**), -621577 (**10a**), -621578 (**10b**), and -621579 (**16**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre at www.ccdc.cam.ac.uk/data_request/cif.

Kinetic Measurements of the Pseudorotation of 9a to 10a

Samples (≈10 mg) of **9a** dissolved in C_6D_6 (0.6 mL) were sealed in an NMR tube under N_2. Kinetic measurements of the pseudorotation process were carried out on a JEOL EX-400 spectrometer by monitoring ^{1}H NMR signals in variable-temperature mode, and the specified temperatures were maintained throughout each set of measurements (error within ±1 °C). The observed temperatures were calibrated with the ^{1}H NMR chemical shift difference in the signals of neat 1,3-propanediol (high-temperature region) and MeOH (low-temperature region). The data were analyzed based on first-order kinetics by using the equation $\ln(C_0/C_{9a})=kT$, in which C_0=ratio of **9a** at t=0, C_{9a}=ratio of **9a** at arbitrary intervals. Here $C_0=C_{9a}+C_{10a}$, $C_0/C_{9a}=(C_{9a}+C_{10a})/C_{9a}=1+1/(C_{9a}/C_{10a})$. The ratio C_{9a}/C_{10a} was monitored by the integration of ^{1}H NMR signals of the methyl group at 50, 55, 60, 65, and 70 °C. Rate constants and activation parameters for stereomutation from **9a** to **10a** are shown in Table 3.

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