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REACTION OF THE □-BENZYLIC ANION OF SPIROPHOSPHORANES WITH *N*,α-DIPHENYLNITRONE: STEREOCHEMISTRY AND FORMATION OF HEXACOORDINATE PHOSPHATE BEARING A 1,2,5-OXAZAPHOSPHOLIDINE RING

Shiro Matsukawa,[a] Yohsuke Yamamoto,[a] and Kin-ya Akiba[b]*

[a] Department of Chemistry, Graduate School of Science, Hiroshima University, 1-3 -1 Kagamiyama, Higashi-Hiroshima 739-8526, Japan

[b] Advanced Research Center for Science and Engineering, Waseda University, 3-4-1 Ohkubo, Shinjuku-ku, Tokyo 169-8555, Japan

e-mail: akibaky@waseda.jp

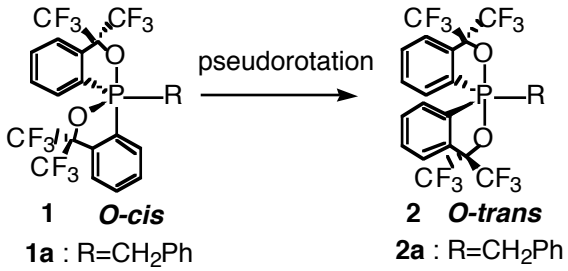
Abstract - The benzylic anion (**3a-Li**) □ to the phosphorus atom generated from *C*-apical *O*-equatorial (*O-cis*) spirophosphorane (**1a**) reacted with *N*,□-diphenylnitrone to give hexacoordinate phosphates (**8**) bearing a 1,2,5-oxazaphospholidine ring. The phosphates were characterized by ^{31}P NMR and by the structure of the products of protonolysis. Examination of the corresponding reactions from *O*-apical *C*-equatorial (*O-trans*) isomer (**2a**) revealed that the phosphates (**9**) derived from **2a** were unstable compared with the hexacoordinated **8** derived from **1a**, mainly due to the stabilizing trans influence of the P-O bond in **8**.

INTRODUCTION

Recently, we reported on the isolation of enantiomeric pairs of optically active 10-P-5 phosphoranes[1] and on the synthesis of spirophosphoranes having an apical carbon-equatorial oxygen array in a five-membered ring (**1**: *O-cis*).[2] The latter represents the first examples of 10-P-5 phosphorane pseudorotamers which violate the apicophilicity concept[3] and can still be converted to their more stable

Dedicated to Prof. Kanaoka on the occasion of his 75th birthday.

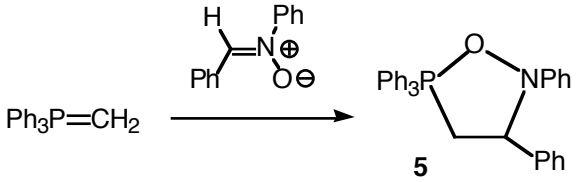
pseudorotamers[4] of apical oxygen-equatorial carbon configuration (**2**: *O-trans*) (Scheme 1). This provided the opportunity to investigate the difference in reactivity between isomeric phosphoranes differing only in stereochemistry upon the pentacoordinate phosphorus atom.[5] The novel spirophosphoranes (*O-cis*) that exhibit anti-apicophilicity showed enhanced reactivity toward nucleophiles such as *n*-$Bu_4N^+F^-$ (TBAF) or MeLi in comparison with their configurationally more stable isomeric *O-trans* counterparts. The enhanced reactivity of the *O-cis* isomer could be explained by the presence of a lower-lying $\sigma^*_{P\text{-}O(equatorial)}$ orbital as the reacting orbital in the equatorial plane whereas the corresponding orbital is a higher-lying $\sigma^*_{P\text{-}C(equatorial)}$ in the *O-trans* isomer. DFT calculations on the actual compounds provided theoretical support for this assumption. In addition, we found that the benzylic anion α to the phosphorus atom in *O-cis* benzyl phosphorane is much more stable than that generated from the corresponding *O-trans* compounds. The experimental results were considered to be due to the $n_C \rightarrow \sigma^*_{P\text{-}O}$ interaction in the *O-cis* anion and this was also confirmed by DFT calculations. Furthermore, the hexacoordinate phosphate derived from the reaction of the benzylic anion from *O-cis* benzylphosphorane with an aldehyde was also found to be well stabilized compared with analogous species from the corresponding *O-trans* isomer and could be characterized by X-Ray structural analysis. This phosphate was shown as a hexacoordinate phosphate intermediate {**11-K(18-crown-6)**} in the Wittig type reaction using pentacoordinate phosphoranes.[5]



Scheme 1

Here we report on the first observation of hexacoordinate phosphates (**8**) bearing a 1,2,5-oxazaphospholidine ring derived from the reaction of the benzylic anion (**3a-M**) from *O-cis* benzylphosphorane (**1a**) with *N*,α-diphenylnitrone. The corresponding reaction of the benzylic anion (**4a-M**) from *O-trans* benzylphosphorane (**2a**) was also examined. Although there have been two reports by Huisgen on the synthesis of 1,2,5-oxazaphospholidines (**5**),[6,7] which were prepared from

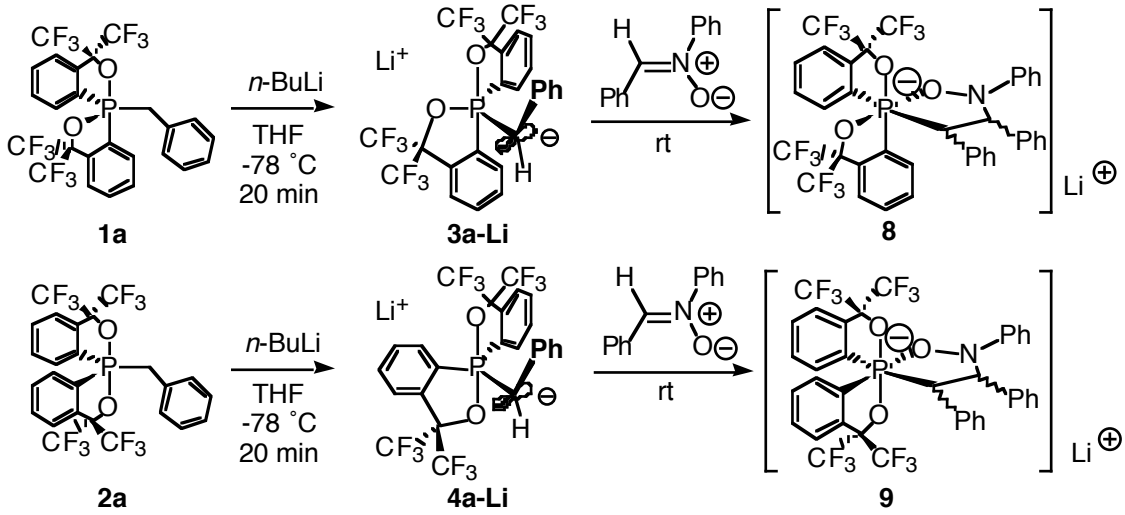
non-stabilized phosphorus ylide with nitrones as shown in Scheme 2, no analogs involving hexacoordinate phosphorus have been known.



Scheme 2

RESULTS AND DISCUSSION

O-cis (**1a**) and *O-trans* benzylphosphorane (**2a**) were easily deprotonated at the position α to the phosphorus atom by *n*-BuLi or KH/18-crown-6 ether in tetrahydrofuran (THF) to afford corresponding α-carbanions (**3a-M**) and (**4a-M**), respectively (Scheme 3).[5] *O-trans* anion (**4a-K(18-crown-6)**) reacted with an equimolar amount of *N*,α-diphenylnitrone at room temperature to afford diastereomeric adducts (**6**) in 67% yield (Table 1) after treatment with water. On the other hand, *O-cis* anion (**3a-K(18-crown-6)**) did not react with the nitrone. The result is consistent with the previous observation that *O-cis* anion (**3a**) is more stable than *O-trans* anion (**4a**) because of the stronger $n \rightarrow \sigma^*_{P\text{-}O}$ interaction in *O-cis* anion (**3a**).[5] However, the corresponding lithium salt *O-cis* anion (**3a-Li**) as well as *O-trans* anion (**4a-Li**) reacted with the nitrone to afford **6** in good yield (Scheme 4 and Table 1). Therefore, since coordination of the lithium cation to nitrone seemed essential for the reaction of **3a**, we employed *n*-BuLi as the base for ensuing investigations as shown below.

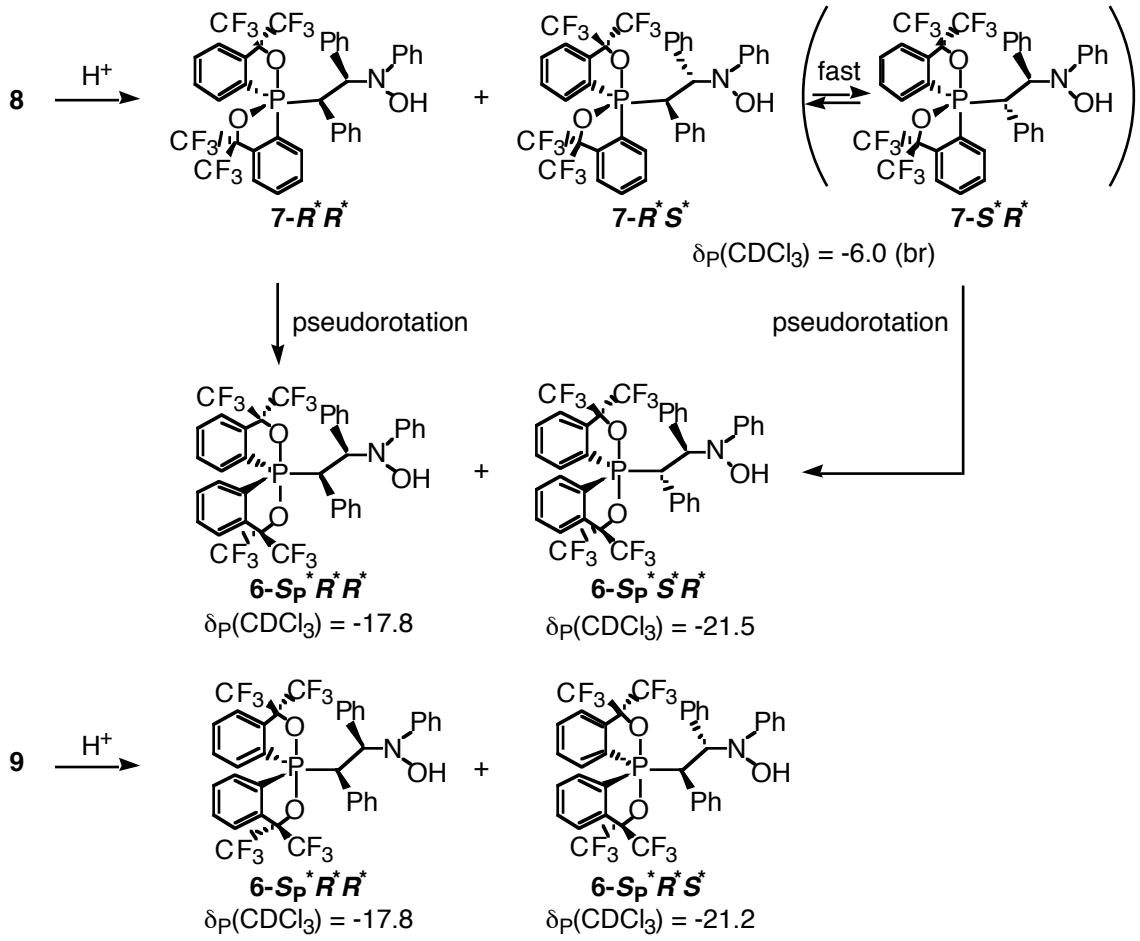


Scheme 3

Table 1. Results of the reactions with *N*,α-diphenylnitrone.

Reactant	Base	Yield (%)	Products Ratio **6-*S*P*R*R*** : **6-*S*P*S*R*** : **6-*S*P*R*S*** : **6-*S*P*S*S***
1a	*n*-BuLi	50	57 : 43 : 0 : 0
1a	KH/18-crown-6	0	—
2a	*n*-BuLi	80	34 : 0 : 66 : 0
2a	KH/18-crown-6	67	15 : 0 : 85 : 0

The relative stereochemistry at the phosphorus is shown as S_P^* throughout this paper.



Scheme 4

The relative stereochemistry between the central phosphorus, the α-carbon and the β-carbon atoms of all three diastereomeric adducts (**6**) was determined by X-Ray crystallographic analysis. The major isomer in the reaction from *O-cis* anion (**3a-Li**) {δP(CDCl3) -17.8 ppm} was determined to be $S_P^*R^*R^*$[8] (Figure 1a), the minor isomer {δP(CDCl3) -21.5 ppm} to be **6-*S*P*S*R*** (Figure 1b), and the major

isomer in reaction from *O-trans* anion (**4a-M**) {δP(CDCl3) -21.2 ppm} was determined to be ***S*P*R*S*** (Figure 1c). The stereochemistry of these products are consistent with our results on the benzoylation of **4a-Li** which afforded a single stereoisomer (***S*P*R***).[5,9] In the reaction of *O-cis* anion (**3a-Li**), we observed the presence of three products by ^{31}P NMR immediately after workup {δP(CDCl3) -6.0 (br), -17.8 and -21.5 (*ca.* 5:10:1)}, but relatively rapid pseudorotation[10] of the compound bearing the chemical shift of -6.0 took place to change into the corresponding *O-trans* isomers. Since the ratio of **6-*S*P*R*R*** {δP(CDCl3) -17.8} and **6-*S*P*S*R*** {δP(CDCl3) -21.5} (ca. 10 : 1) in the crude mixture changed to **6-*S*P*R*R*** : **6-*S*P*S*R*** = 57 : 43 upon disappearance of the assumed *cis* compound {δP(CDCl3) -6.0}, it can be derived that this *cis* compound converted to the *trans* compound of **6-*S*P*S*R***. This is in agreement with a similar conversion in the bromination at the α-position of *O-cis* **1a**, which provided *O-trans* brominated product (**10-*S*P*R***) stereoselectively (Scheme 5).[5] The configuration of the *cis* compound can be assigned ***R*S****[11] (Scheme 4).

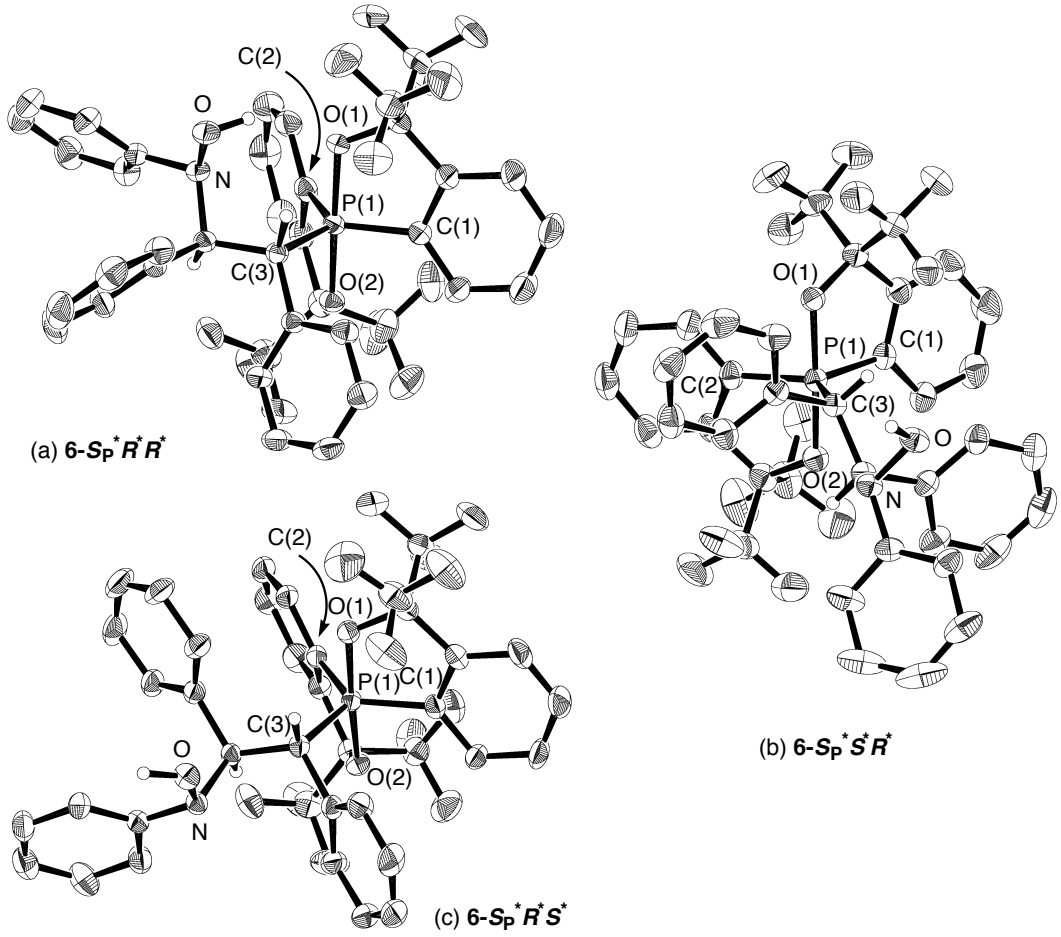
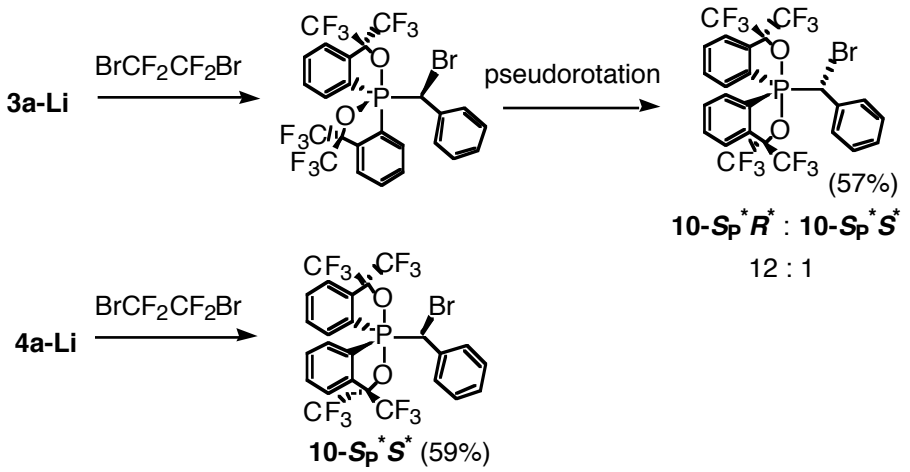


Figure 1. *ORTEP* drawings of (a) **6-*S*P*R*R***, (b) **6-*S*P*S*R***, and (c) **6-*S*P*R*S*** showing the thermal ellipsoids at the 30% probability level.



Scheme 5

In order to detect the formation of the reaction intermediates (**8** and **9**), which were assumed to be hexacoordinate phosphates bearing a 1,2,5-oxazaphospholidine ring, the reaction of *O-cis* anion (**3a-Li**) {δP(THF) +2} with the nitrone was monitored (Figure 2). ^{31}P NMR of the reaction mixture showed the two highly upfield-shifted signals {δP(THF) -110 (**8A**) and -107 (**8B**); ratio *ca.* 2:3}. These results strongly indicated that the two intermediates (**8A** and **8B**) were hexacoordinate phosphates bearing an 1,2,5-oxazaphospholidine ring since significant upfield shift (around δP -100 ~ -150) has been known to be an indicator for the formation of hexacoordinated form.[3,12] After the reaction was treated with water, the mixture of **6-*S*P**R**R**** and **6-*S*P**S**R**** was obtained with essentially the same ratio of 57 : 43 (ca. 3 : 2) as shown in Table 1. Coupled with the fact that steric repulsion between α-phenyl and a CF_3 group of the Martin ligand with the apical carbon atom in species where the stereochemistry upon phosphorus is inverted should disfavor such configurations, the stereochemisy of **8A** and **8B** should correspond to the structures illustrated in Figure 2.

In the reaction of the corresponding *O-trans* (**4a-Li**) {δP(THF) -34}, two signals were also observed {δP(THF) -84 (**9B**, br) and -19 (**9A**); ratio *ca.* 1:2}. Since the ratio is similar to the product ratio of **6-*S*P**R**R**** and **6-*S*P**R**S**** (34 : 66), the structure of **9B** and **9A** correspond to species arising from **6-*S*P**R**R**** and **6-*S*P**R**S****, respectively. The signal for **9A** appeared in a remarkably downfield-shifted region compared with those for the other three signals (**8A**, **8B**, and **9B**). This implied that **9A** was a pentacoordinate phosphorane where the oxazaphospholidine ring is opened. The reason for this preference for the pentacoordinate state is probably because of the steric repulsion between the two phenyl

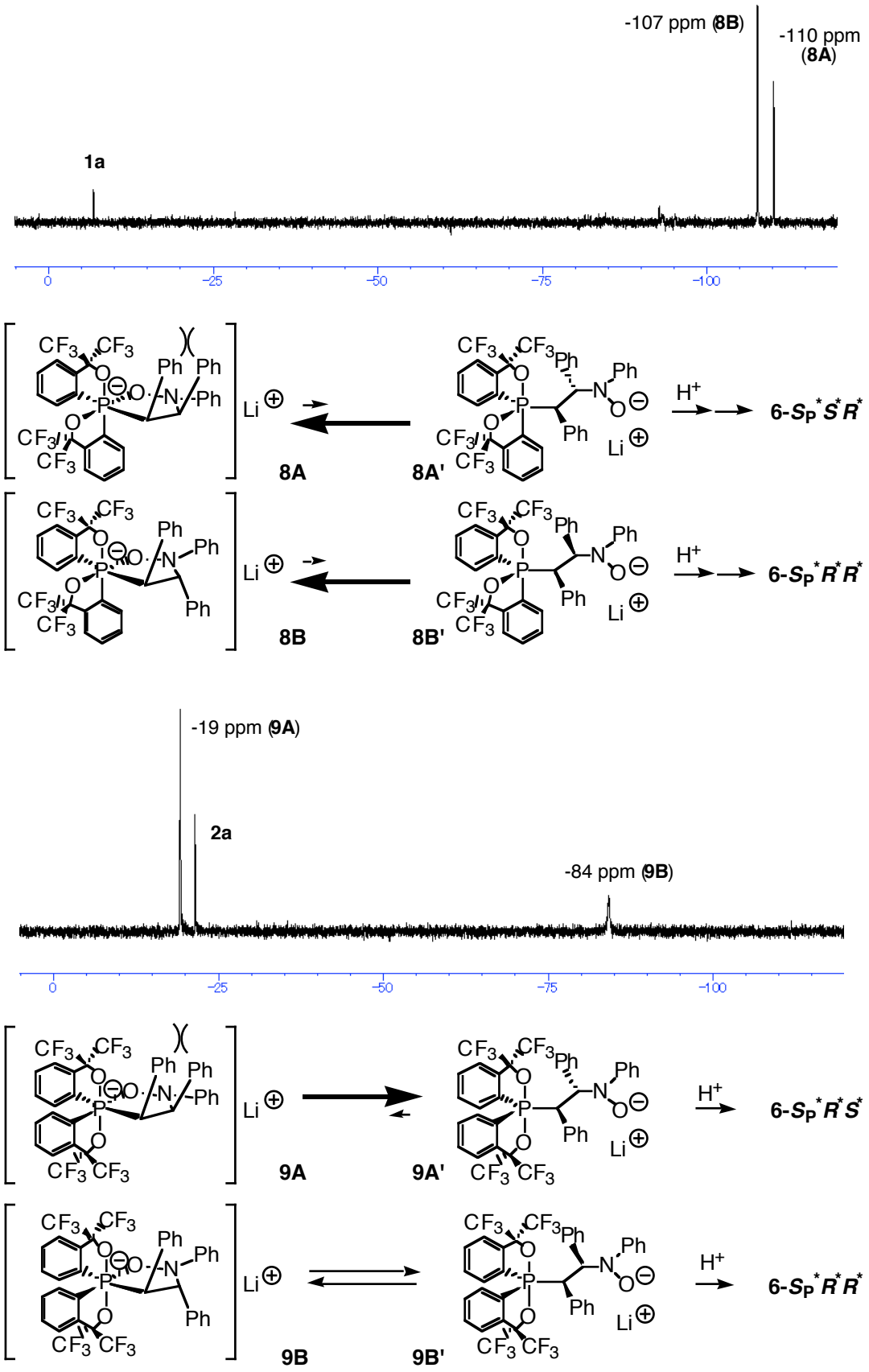
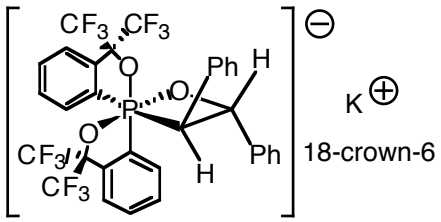


Figure 2. ^{31}P NMR of the reaction mixture of **3a-Li** and **4a-Li** with *N*,α-diphenylnitrone

groups in the hexacoordinate form. In addition, the signal for **9B** (-84 ppm) was broadened and moderately downfield-shifted (by *ca*. 20 ppm) in comparison with **8A** and **8B**, and this certainly indicates that **9B** is in an equilibrium between the pentacoordinate and the hexacoordinate state. These results show clearly that the hexacoordinate forms are less stable in **9**, derived from *O-trans* (**4a-Li**), in comparison with those of **8**, derived from the corresponding *O-cis* (**3a-Li**). This tendency is rationalized by the two kinds of effects of the Martin ligand written in the lower sphere in **8** and **9**, i.e., (i) trans influence of P-O bond to stabilize the oxazaphospholidine ring in **8**, (ii) smaller steric hindrance to the oxazaphospholidine ring effected by the CF_3 group (in **8**). In the case of **9A**, the oxazaphospholidine ring is opened almost by the added steric hindrance between the two parallel phenyl rings. The result is consistent with our previous observations where a hexacoordinate Wittig-type intermediate {**11-K(18-crown-6)**} derived from *O-cis* anion (**3a**) was isolated stable and characterized by X-Ray analysis[5] whereas the corresponding hexacoordinate phosphates derived from **4a** decomposed easily even at -40 °C.[9a,b]



11-K(18-crown-6)

In summary, we have demonstrated the formation of hexacoordinate phosphates bearing a 1,2,5-oxazaphospholidine ring (**8** and **9**) derived by the reaction of *O-cis* anion (**3a-Li**) and *O-trans* anion (**4a-Li**) with *N*,α-diphenylnitrone. The fact that the former was more stable than the latter demonstrates the effect of trans influence of the equatorial P-O bond in the *O-cis* framework. Further investigations are ongoing.

EXPERIMENTAL

General.

Melting points were measured with a Yanaco micro melting point apparatus and are uncorrected. ^{1}H NMR (400 MHz), ^{19}F NMR (376 MHz), and ^{31}P NMR (162 MHz) spectra were recorded on a JEOL EX-400 spectrometer. ^{1}H NMR chemical shifts (δ) are given in ppm downfield from Me_4Si, determined by residual chloroform (δ = 7.26). ^{19}F NMR chemical shifts (δ) are given in ppm downfield from external $CFCl_3$. ^{31}P NMR chemical shifts (δ) are given in ppm downfield from external 85% H_3PO_4. Elemental analyses were performed on a Perkin-Elmer 2400 CHN elemental analyzer.

All reactions were carried out under N_2 or Ar. THF was freshly distilled from Na-benzophenone. Preparative thin layer chromatography was carried out on plates of Merck silica gel 60 GF_{254}.

Reaction of the α-anion of 1a (3a-Li) with *N*,α-diphenylnitrone.

To a THF (3 mL) solution of **1a** (186 mg, 0.307 mmol) was added *n*-BuLi (1.57 M hexane solution, 0.21 mL, 0.32 mmol) at 0 ˚C. The mixture was stirred for 15 min at 0 ˚C, then a THF (1 mL) solution of *N*,α-diphenylnitrone (63 mg, 0.32 mmol) was added. The mixture was stirred for 6 h at rt, then the reaction was quenched with saturated aqueous NH_4Cl. The mixture was extracted with Et_2O (50 mL), and the extract was washed with brine (50 mL) and dried over anhydrous $MgSO_4$. After removing solvents by evaporation, the crude product was separated by TLC (*n*-hexane : CH_2Cl_2 = 3 : 2) to afford a pale yellow solid of **6-*S*P**S**R**** (53.3 mg, 21.6%) and **6-*S*P**R**R**** (70.6 mg, 28.6%). Colorless crystals of **6-*S*P**S**R**** suitable for X-Ray analysis were obtained by recrystallization from *n*-hexane/CH_2Cl_2. **6-*S*P**S**R**** : ^{1}H NMR ($CDCl_3$, δ) 7.61-6.73 (m, 23H), 5.39 (dd, 1H, $J_{P\text{-}H}$= 11.5 Hz, $^{3}J_{H\text{-}H}$= 11.5 Hz), 4.83 (dd, 1H, $J_{P\text{-}H}$= 20.0 Hz, $^{3}J_{H\text{-}H}$= 11.5 Hz); ^{19}F NMR ($CDCl_3$, δ) – 72.4 (br s, 3F), -73.9 (br s, 6F),-75.5 (br s, 3F); ^{31}P NMR ($CDCl_3$, δ) -21.5; mp 199-201 ˚C. Colorless crystals of **6-*S*P**R**R**** suitable for X-Ray analysis were obtained by recrystallization from *n*-hexane/CH_2Cl_2. **6-*S*P**R**R**** : ^{1}H NMR ($CDCl_3$, δ) 8.44-8.39 (m, 1H), 7.79-7.77 (m, 2H), 7.71-7.67 (m, 1H), 7.61-7.57 (m, 1H), 7.46-7.36 (m, 3H), 7.05-6.86 (m, 8H), 6.83-6.74 (m, 4H), 6.63 (s, 1H), 6.19 (d, 1H, *J* = 5.4 Hz), 6.09 (d, 2H, *J* = 7.8 Hz), 5.12 (dd, 1H, $J_{P\text{-}H}$ = 12.9 Hz, $^{3}J_{H\text{-}H}$ = 12.9 Hz), 5.04 (dd, 1H, $J_{P\text{-}H}$ = 12.9 Hz, $^{3}J_{H\text{-}H}$ = 12.9 Hz); ^{19}F NMR ($CDCl_3$, δ) -73.0 (q, 3F, $^{4}J_{F\text{-}F}$ = 9.8 Hz), -73.9 (q, 3F, $^{4}J_{F\text{-}F}$ = 9.8 Hz),-74.2 (q, 3F, $^{4}J_{F\text{-}F}$ = 9.2 Hz),-74.6 (q, 3F, $^{4}J_{F\text{-}F}$ = 9.2 Hz);

^{31}P NMR ($CDCl_3$, δ) -17.8; mp 202-204 ℃; Anal. Calcd for $C_{38}H_{26}NO_3F_{12}P$: C, 56.79; H, 3.26; N, 1.74. Found: C, 56.60; H, 3.06; N, 1.68.

Reaction of the α-anion of 2a (4a-Li) with *N*,α-diphenylnitrone.

To a THF (3 mL) solution of **2a** (183 mg, 0.301 mmol) was added *n*-BuLi (1.57 M hexane solution, 0.22 mL, 0.33 mmol) at 0 ℃. The mixture was stirred for 15 min at 0 ℃, then a THF (1 mL) solution of *N*,α-diphenylnitrone (66.5 mg, 0.337 mmol) was added. The mixture was stirred for 1 h at rt, then the reaction was quenched with saturated aqueous NH_4Cl. The mixture was extracted with Et_2O (50 mL), and the extract was washed with brine (50 mL) and dried over anhydrous $MgSO_4$. After removing solvents by evaporation, the crude product was separated by TLC (*n*-hexane : CH_2Cl_2 = 2 : 1) to afford a pale yellow solid of **6-*S*P**R**R*** (65.9 mg, 27.2%) and an orange solid of **6-*S*P**R**S*** (128 mg, 53.1%). **6-*S*P**R**S*** : ^{1}H NMR ($CDCl_3$, δ) 7.90 (br s, 1H), 7.60-6.75 (m, 21H), 6.73 (s, 1H), 5.11 (dd, 1H, J_{P-H} = 12.0 Hz, $^3J_{H-H}$ = 12.0 Hz), 4.87 (dd, 1H, J_{P-H} = 15.4 Hz, $^3J_{H-H}$ = 12.0 Hz), 4.15 (s, 1H); ^{19}F NMR ($CDCl_3$, δ) -72.5 (br s, 3F), -74.2 (br s, 6F), -75.1 (br s, 3F); ^{31}P NMR ($CDCl_3$, δ) -21.2; mp 185-187 ℃.

X-Ray structural determinations of 6-*S*PR**R*, 6-*S*P**R**S*, and 6-*S*P**S**R*.**

Crystals suitable for X-Ray structural determination were mounted on a Mac Science DIP2030 imaging plate diffractometer and irradiated with graphite-monochromated Mo *Kα* radiation (λ = 0.71073 Å) for data collection. Unit cell parameters were determined by autoindexing several images in each data set separately with the DENZO program (Mac Science).[13] For each data set, rotation images were collected in 3 ° increments with a total rotation of 180 ° about the ϕ axis. Data were processed by using SCALEPACK.

The structure was solved by a direct method with the SIR-92 program. Refinement of *F* was carried out by full-matrix least-squares. All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were included in the refinement with isotropic thermal parameters. The crystallographic data are summarized in Table 2. Selected bond lengths and angles are summarized in Table 3.

Table 2. Crystallographic data for **6-*S*P**R***R****, **6-*S*P**R***S**** and **6-*S*P**S***R****

Compound	**6-*S*P**R***R****	**6-*S*P**R***S****	**6-*S*P**S***R****
Formula	$C_{38}H_{26}NO_3F_{12}P$	$C_{38}H_{26}NO_3F_{12}P$	$C_{38}H_{26}NO_3F_{12}P$
Mot wt	803.58	803.58	803.58
Cryst syst	Triclinic	Triclinic	Triclinic
Space group	*P*-1	*P*-1	*P*-1
Color	colorless	colorless	colorless
Habit	prism	plate	plate
Cryst dimens, mm	0.50 x 0.40 x 0.30	0.50 x 0.40 x 0.30	0.40 x 0.30 x 0.10
a, Å	10.7210(4)	11.0820(5)	10.6380(5)
b, Å	12.2830(4)	11.4350(5)	12.2540(5)
c, Å	14.9130(5)	14.6300(4)	13.7910(6)
α, deg	87.110(2)	78.187(3)	94.706(3)
β, deg	82.161(2)	76.024(3)	92.754(2)
γ, deg	64.822(2)	82.905(2)	91.195(3)
V, Å^3	1760.6(1)	1755.6(1)	1789.1(1)
Z	2	2	2
D_{calc}, g cm^{-3}	1.516	1.520	1.492
Abs coeff, mm^{-1}	0.181	0.182	0.178
F(000)	816	816	816
Radiation; λ, Å	Mo $K\alpha$; 0.71073	Mo $K\alpha$; 0.71073	Mo $K\alpha$; 0.71073
Temp, K	298	298	298
Data collcd	$+h, \pm k, \pm l$	$+h, \pm k, \pm l$	$+h, \pm k, \pm l$
Total data collcd,	7558	7261	7899
unique,	7558	7251	7899
obsd	6446 ($I > 3\sigma(I)$)	6153 ($I > 3\sigma(I)$)	6070 ($I > 3\sigma(I)$)
No of params refined	496	496	496
R	0.0600	0.1492	0.0592
R_W	0.1084	0.2374	0.0959
GOF	1.389	2.288	1.122
Max shift in final cycle	0.0011	0.0001	0.0000
Final diff map, max, e/Å	0.18	1.06	0.21
Solv for crystallization	*n*-hexane/CH_2Cl_2	*n*-hexane/CH_2Cl_2	*n*-hexane/CH_2Cl_2

Table 3. Selected bond lengths (Å) and angles (deg).

	6-*S*PR***R****	**6-*S*P**R***S****	**6-*S*P**S***R****
P(1)—O(1)	1.790(1)	1.756(3)	1.757(2)
P(1)—O(2)	1.748(1)	1.766(3)	1.774(2)
P(1)—C(1)	1.819(2)	1.818(5)	1.826(2)
P(1)—C(2)	1.824(2)	1.826(5)	1.816(2)
P(1)—C(3)	1.875(2)	1.864(5)	1.865(2)
O(1)—P(1)—O(2)	176.79(6)	173.9(2)	176.13(7)
O(1)—P(1)—C(1)	86.90(7)	87.2(2)	86.80(9)
O(1)—P(1)—C(2)	90.47(8)	89.9(2)	92.70(9)
O(1)—P(1)—C(3)	91.37(7)	92.6(2)	94.91(8)
O(2)—P(1)—C(1)	92.63(8)	91.7(2)	90.39(9)
O(2)—P(1)—C(2)	87.15(8)	86.0(2)	86.76(8)
O(2)—P(1)—C(3)	91.74(7)	93.3(2)	88.77(7)
C(1)—P(1)—C(2)	123.79(8)	127.5(2)	125.42(9)
C(1)—P(1)—C(3)	113.01(8)	112.6(2)	118.74(9)
C(2)—P(1)—C(3)	123.19(8)	119.9(2)	115.67(9)

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REFERENCES AND NOTES

1 (a) S. Kojima, K. Kajiyama, and K.-y. Akiba, *Tetrahedron Lett.,* 1994, **35**, 7037. (b) S. Kojima, K. Kajiyama, and K.-y. Akiba, *Bull. Chem. Soc. Jpn.,* 1995, **68**, 1785.

2 (a) S. Kojima, K. Kajiyama, M. Nakamoto, and K.-y. Akiba, *J. Am. Chem. Soc.*, 1996, **118**, 12866. (b) K. Kajiyama, M. Yoshimune, M. Nakamoto, S. Matsukawa, S. Kojima, and K.-y. Akiba, *Org. Lett.,* 2001, **3**, 1873.

3 (a) K.-y. Akiba, 'Chemistry of Hypervalent Compounds,' Wiley-VCH, New York, 1999. (b) R. R. Holmes, 'Pentacoordinated Phosphorus—Structure and Spectroscopy,' ACS Monograph 175, 176, Vol. I, II, American Chemical Society, Washington, DC, 1980.

4 see some compounds which violate the concept of apicophilicity. In these cases some sort of steric constraints disallowed regular configurations. (a) N. V. Timosheva, T. K. Prakasha, A. Chandrasekaran, R. O. Day, and R. R. Holmes, *Inorg. Chem.*, 1995, **34**, 4525. (b) N. V.

Timosheva, A. Chandrasekaran, T. K. Prakasha, R. O. Day, and R. R. Holmes, *Inorg. Chem.*, 1996, **35**, 6552. (c) S. Vollbrecht, A. Vollbrecht, J. Jeske, P. G. Jones, R. Schmutzler, and W.-W. du Mont, *Chem. Ber./Recl/* 1997, **130**, 819.

5 S. Matsukawa, S. Kojima, K. Kajiyama, Y. Yamamoto, K.-y. Akiba, S. Re, and S. Nagase, *J. Am. Chem. Soc.*, 2002, **124**, 13154.

6 R. Huisgen and M. Christ, *Angew. Chem., Int. Ed. Engl.,* 1967, **6**, 456.

7 R. Huisgen and J. Wulff, *Chem. Ber.,* 1969, **102**, 746.

8 The stereochemical denotations correpond (in the written order) to the phosphorus atom, the carbon α to the phosphorus and the carbon atom β to the phosphorus, respectively. For proposed nomenclature for the pentacoordinated phosphorus atom see: J. C. Martin and T. M. Balthazor, *J. Am. Chem. Soc.*, 1977, **99**, 152.

9 (a) S. Kojima, K. Kawaguchi, and K.-y. Akiba, *Tetrahedron Lett.,* 1997, **38**, 7753. (b) S. Kojima, K. Kawaguchi, S. Matsukawa, and K.-y. Akiba, *Tetrahedron*, 2003, **59**, 255.

10 R. S. Berry, *J. Chem. Phys.,* 1960, **32**, 933.

10 We already reported that one-step pseudorotation at the phosphorus atom of *O-cis* spirophosphoranes with a monodentate ligand is rapid (ref. 2a and 5). Compound (**7**) likewise existed as a rapidly equilibrating mixture of **7-*S*P**S***R**** and **7-*R*P**S***R**** (=**7-*S*P**R***S****).

12 (a) R. Engel, 'Handbook of Organophosphorus Chemistry,' Marcel Dekker, New York, 1992. (b) D. E. C. Corbridge, 'Phosphorus: An Outline of Its Chemistry, Biochemistry, and Technology,' 4th ed., Elsevier: Amsterdam, 1990, Chapter 14; pp. 1233-1256. (c) R. Burgada and R. Setton, 'The Chemistry of Organophosphorus Compounds,' Vol. 3, ed. by F. R. Hartley, Wiley-Interscience: Chichester, 1994, pp. 185-272. (d) A. C. Hengge, *Acc. Chem. Res.,* 2002, **35**, 105 and references therein.

13 Z. Otwinowski, University of Texas, Southwestern Medical Center.