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Synthesis and Reactions of Diphosphenes Carrying Bulky Aryl and Phenoxy Groups

De-Lie An, Kozo Toyota, Masafumi Yasunami, and Masaaki Yoshifuji*

Department of Chemistry, Faculty of Science, Tohoku University, Aoba, Sendai 980-77, Japan

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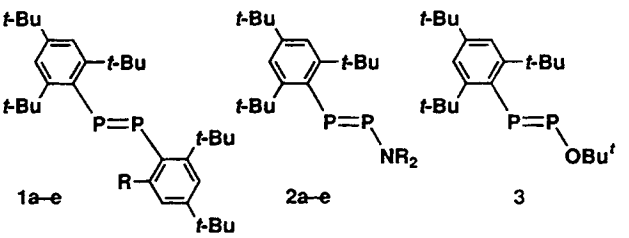
ABSTRACT

Unsymmetrical diphosphenes carrying bulky aryl and phenoxy groups were prepared by the reaction of lithium 2,4,6-tri-t-butylphenylphosphide with the corresponding phenyl phosphorodichloridites, followed by the dehydrochlorination reaction with 1,8-diazabicyclo[5.4.0]undec-7-ene. The diphosphenes were isolated as stable compounds. The reactions of these diphosphenes with elemental sulfur or selenium afforded the corresponding thiadiphosphiranes or selenadiphosphiranes, respectively. The diphosphenes also reacted with dichlorocarbene to give dichlorodiphosphiranes.



1 a: R = *t*-Bu, **b**: R = Me, **c**: R = NMe_2, **d**: R = OMe, **e**: R = CH_2OMe; **2 a**: R = *c*-C_6H_{11}, **b**: NR_2 = 2,2,6,6-Me_4piperidino, **c**: NR_2 = NTms-($NTms_2$); **d**: R = Tms; **e**: NR_2 = N(Mesityl)(9-Fluorenyl).

CHART 1

INTRODUCTION

Physicochemical properties of low coordinated phosphorus compounds such as diphosphenes are of current interest. We have previously reported the preparation, characterization, and crystal structure of 1,2-bis(2,4,6-tri-*t*-butylphenyl)diphosphene (**1a**) using the 2,4,6-tri-*t*-butylphenyl group (abbreviated as Ar) as a sterically protecting group [1]. Moreover, we have prepared several diphosphenes **1b–e** with the Ar group and other protecting groups such as 2,4-di-*t*-butyl-6-methylphenyl [2], 2,4-di-*t*-butyl-6-(dimethylamino)phenyl [3], 2,4-di-*t*-butyl-6-(methoxy)phenyl [4], and 2,4-di-*t*-butyl-6-(methoxymethyl)phenyl [5]. In the diphosphenes **1c–e**, one of the *o*-*t*-butyl groups in the Ar groups of **1a** is replaced by electron-donating dimethylamino, methoxy, and methoxymethyl groups, respectively.

We and others have also described some diphosphenes **2** with the >N–P=P– skeleton [6–8]. However, reports on diphosphenes containing the –O–P=P– structure have been limited. Only the preparation and ^{31}P NMR chemical shift for 1-*t*-butoxy-2-(2,4,6-tri-*t*-butylphenyl)diphosphene (**3**) were reported by Markovski *et al.* [8]. No stable compounds of this type have been reported so far, although some transition-metal complexes including the –O–P=P– skeleton have been described [9,10].

It is of interest to compare the properties of the diphosphenes carrying the –O–P=P– system with those of the diphosphenes **1** or **2**. In this article, we wish to report the preparation and properties of the stable diphosphenes with the –O–P=P– skeleton [11].

Dedicated to Prof. Shigeru Oae on the occasion of his seventy-fifth birthday.

*To whom correspondence should be addressed.

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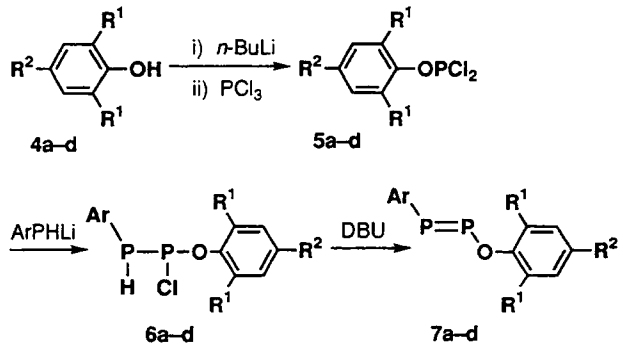


a: $R^1 = R^2 = t$-Bu; **b**: $R^1 = t$-Bu, R^2 = Me; **c**: $R^1 = t$-Bu, R^2 = H; **d**: $R^1 = s$-Bu, R^2 = H; DBU = 1,8-diazabicyclo[5.4.0]undec-7-ene.

SCHEME 1

RESULTS AND DISCUSSION

Synthesis of Diphosphenes

Sterically hindered phenyl phosphorodichloridites **5a–d** were prepared from the corresponding phenols **4a–d**. Reaction of **5a–d** with lithium 2,4,6-tri-*t*-butylphenylphosphide [12], followed by the dehydrochlorination reaction of the resulting chlorodiphosphanes **6a–d** [13] with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), gave the corresponding unsymmetrical diphosphenes **7a–d** (Scheme 1). Diphosphenes **7a–c** were stable toward air and moisture, while **7d** decomposed during the silica-gel column-chromatographic procedure, indicating that the bulk at the *o*-position in the phenoxy group plays an important role in stabilization of diphosphenes of this type. Attempts to prepare the symmetrical diphosphene ArO–P=P–OAr, however, by the reaction of phenyl phosphorodichloridite **5a** with either magnesium or lithium naphthalenide were unsuccessful. It seems likely that steric hindrance or the electronic factor is not efficient enough for stabilization of the symmetrical diphosphenes.

Table 1 shows the ^{31}P NMR data of **7** together with some related diphosphenes **1**, **2**, and **3**, where P^A denotes the Ar-substituted phosphorus atom and P^B denotes the other phosphorus atom, except for the symmetrical **1a**. The ^{31}P NMR spectra of the diphosphenes **7a–d** showed an AB pattern, unequivocally characteristic of unsymmetrical diphosphenes. The signals due to the P^A of the diphosphenes **7a–d** appear at slightly higher field (δ_P 409–412) compared with those for **1a** (δ_P 490). The phenoxy-group substituted phosphorus atoms (P^B) of **7a–d** resonate at significantly low field (δ_P 526–535) compared with the P^A for **7a–d** or P^A for **1a**. These facts can be interpreted by considering resonance structures of the –O–P=P– π system involving the P=P double bond perturbed by the lone-pair electrons of the oxygen atom similarly to the case of the >N–P=P– π system [6,7]. The contribution of a zwitterionic structure seems to be important in the –O–P=P– π system as well as in the >N–P=P– π system, since the ^{31}P NMR chemical-shift differences between P^A and P^B ($\Delta\delta_P$) for **2** and for **7** are large.

Reaction of the Diphosphenes with Sulfur or Selenium

The reactions of **7a–c** with elemental sulfur at room temperature in pyridine led to the formation of the corresponding thiadiphosphiranes **8a–c** (Scheme 2). All these three-membered ring compounds were stable toward air and moisture. We have already reported the reaction of **1a** with elemental sulfur giving diphosphene monosulfide **9**, which was rearranged to the corresponding thiadiphosphirane **10a** by heat or light [14]. During the reaction of the diphosphene **7a** with elemental sulfur, a set of weak transient signals of an AB pattern were observed at δ_P 98.7 and 253.6 with J_{PP} = 730.5 Hz by ^{31}P NMR spectroscopy, and the signals disappeared in a few hours. The fact that the δ_P value and the spin-spin coupling constant (J_{PP}) are similar to those for **9** (δ_P 247.8 and 255.8, $^1J_{PP}$ = 629.9 Hz) indicates that these signals might be due to **12A** or **12B**, although attempted isolation of the intermediate was unsuccessful.

We have already investigated formation of selenadiphosphiranes **14a–c** from the corresponding diphosphenes and selenium [15]. Very similarly, the reaction of **7a–c** with elemental selenium in benzene in the presence of pyridine at 60°C afforded the corresponding selenadiphosphiranes **13a–c** (Scheme 2). The compound **13a** was isolated by column chromatography as stable colorless crystals in 37% yield, although **13b** and **13c** were not stable enough to permit isolation by a similar method to that employed for **13a**.

Table 2 and Table 3 show the ^{31}P NMR data of the thiadiphosphiranes, **8**, **10**, and **11**, and selenadiphosphiranes, **13** and **14**, respectively, where P^A denotes the Ar-substituted phosphorus atom and P^B denotes the other phosphorus atom, except for **10** and **14**.

In Table 2, the aromatic-group substituted phosphorus atoms appear at higher field (δ_P −65 to −114), which is characteristic of phosphiranes, while the phenoxy- or amino-substituted P^B atoms appear at lower field (δ_P 52 to −5) similarly to the case of diphosphenes, as listed in Table 1. In Table 3, a significant downfield shift for **13** in comparison to **8** was observed, and the fact can be ascribed to the widening of the P–P–Se angles compared to the P–P–S angles [16]. Furthermore, a big difference between $^1J_{PA_{Se}}$ and $^1J_{PB_{Se}}$ in magnitude in **13** was

TABLE 1 ^{31}P NMR Data of Diphosphenes **7**, **1**, **2**, and **3**

Compound[a]	δ_{P^A}	δ_{P^B}	$\Delta\delta_P$ *(ppm)*[b]	$^1J_{PP}$ *(Hz)*	*Solvent*	*Reference*
1a	490.0[c]		0	—	$CDCl_3$	[1]
1b	480.1	517.0	36.9	583.5	C_6D_6	[2]
2a	270.2	448.8	178.6	543.5	$CDCl_3$/THF	[6a]
2b	336.1	460.7	124.6	579.9	THF	[7a]
2c	311	481	170	554	C_6D_6	[7b]
2d	409.3	501.5	92.2	584.2	Hexane	[7a]
2e	310.3	452.1	141.8	544.1	$CDCl_3$	[6b]
3	397.6	524.3	126.7	573.7	Et_2O	[8]
7a	409.8	534.1	124.3	572.2	$CDCl_3$	this work
7b	409.7	534.4	124.7	572.3	$CDCl_3$	this work
7c	410.4	533.2	122.8	572.5	$CDCl_3$	this work
7d	411.8	526.1	114.3	578.9	C_6D_6	this work

[a] P^A denotes the Ar-substituted phosphorus atom and P^B denotes the other except for **1a**.
[b] $\Delta\delta_P$ denotes the chemical-shift difference between δ_{P^A} and δ_{P^B} in ppm.
[c] δ_P value in C_6D_6 for **1a**: 492.4 [1].

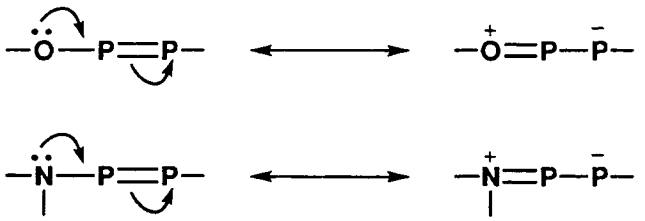
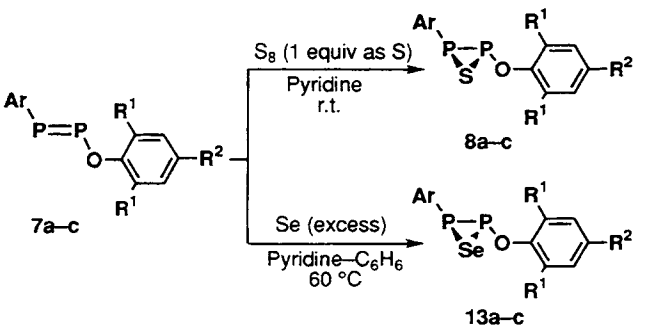


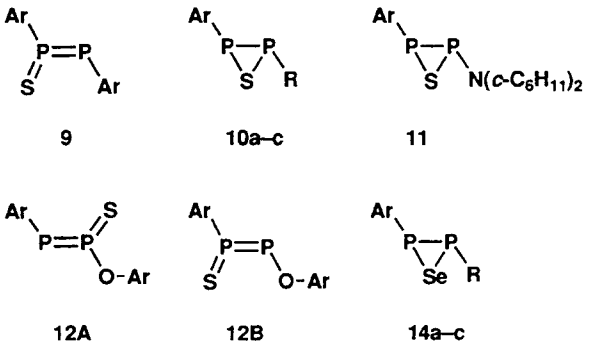
CHART 2

observed. It is plausible that the P^A atom is of the sp^3 or p^3 configuration, while the P^B atom has an sp^2 character to some extent because of the mesomeric contribution of the oxygen lone pair; thus, the P^B–Se bond is shorter (or consisting of much s-character) than the P^A–Se bond, resulting in the increased coupling constant $^1J_{P^BSe}$. The larger coupling constants $^1J_{PP}$ for **13** compared to those for **8** might also be due to the increased s-character in the P–P bond of **13**.



a: $R^1 = R^2 = t$-Bu; **b**: $R^1 = t$-Bu, R^2 = Me; **c**: $R^1 = t$-Bu, R^2 = H.

SCHEME 2



10 a: R = Ar, **b**: R = 2,4-*t*-Bu_2-6-MeC_6H_2, **c**: R = 2,4-*t*-Bu_2-6-(MeO)-C_6H_2;
14 a: R = Ar, **b**: R = Mesityl, **c**: R = 2,4-*t*-Bu_2-6-(MeO)C_6H_2.

CHART 3

Reaction of the Diphosphene with Dichlorocarbene

Furthermore, we investigated the reaction of diphosphene **7a** with dichlorocarbene. We and others have reported the reaction of the diphosphene **1a** with dichlorocarbene to give 3,3-dichloro-1,2-bis(2,4,6-tri-*t*-butylphenyl)-1,2-diphosphirane, which was converted to 1,3-diphosphaallene by treatment with methyllithium or *t*-butyllithium [17]. When the diphosphene **7a** was allowed to react with dichlorocarbene, an expected 3,3-dichloro-1,2-diphosphirane **16a** was obtained (in 32% isolated yield). Although the mechanism for the formation of **16a** has not yet been confirmed, we suggest, as a plausible mechanism, that it might involve the initial addition of electrophilic dichlorocarbene to one of the phosphorus atoms (probably at P^A because it is more electron rich) to produce an in-

TABLE 2 ^{31}P NMR Data of Thiadiphosphiranes **8**, **10**, and **11** in $CDCl_3$

Compound[a]	δ_{PA}	δ_{PB}	$^1J_{PP}$ *(Hz)*
8a	−91.3	51.5	274.5
8b	−90.7	51.5	274.7
8c	−91.2	52.0	274.4
10a[b]	−65.1		—
10b[c]	−72.5	−67.0	245.4
10c[d,e]	−81.8	−67.6	247.0
11[f]	−113.7	−4.7	251.1

[a]P^A denotes the Ar-substituted phosphorus atom and P^B denotes the other except for **10**.
[b]Data taken from Ref. [14a].
[c]Data taken from Ref. [14c].
[d]NMR data measured in C_6D_6.
[e]Data taken from Ref. [4].
[f]Data taken from Ref. [6a].

termediate **15a**, followed by rearrangement to **16a**. It should be noted that AB pattern signals at δ_P 166.8 and 303.5 ppm with J_{PP} = 308.3 Hz were observed in the ^{31}P NMR spectra taken during the reaction. The signals of this AB pattern may be due to an intermediate **15a** with a >C=P(=P–)– framework [18], since the ^{31}P chemical shift is similar to those for the compounds with the >C=P(=X)– (X = NR or S) species [19,20]. Moreover, the value of spin-spin coupling (J_{PP}) of the intermediate indicates the phosphorus—phosphorus double bond. An attempted conversion of **16a** to the corresponding 1,3-diphosphaallene [17] by addition of *t*-butyllithium was unsuccessful.

In summary, bulky phenols, readily available as radical inhibitors turned out to be effective to stabilize low coordinated phosphorus compounds such as diphosphenes. These bulky phenols and the diphosphenes thus stabilized might become useful reagents in novel heteroatom chemistry.

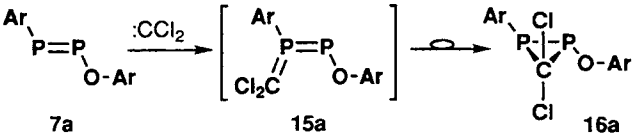
EXPERIMENTAL

All experiments were carried out under an argon atmosphere with dry solvents, unless otherwise

TABLE 3 ^{31}P NMR Data of Selenadiphosphiranes **13** and **14** in $CDCl_3$

Compound[a]	δ_{PA}	δ_{PB}	$^1J_{PP}$ *(Hz)*	$^1J_{PASe}$ *(Hz)*	$^1J_{PBSe}$ *(Hz)*
13a	−65.2	76.6	289.0	103.0	236.2
13b	−63.4	76.9	289.1	102.2	235.0
13c	−64.0	77.8	288.9	104.4	236.3
14a[b]	−47.7		—	131.8	
14b[b]	−69.2	−72.0	246.6	—[c]	—[c]
14c[d]	−47.5	−66.0	260.4	115.9	120.1

[a]P^A denotes the Ar-substituted phosphorus atom and P^B denotes the other except for **14**.
[b]Data taken from Ref. [15a].
[c]$^1J_{PSe}$ values not reported.
[d]Data taken from Ref. [15b].



7a 15a 16a

SCHEME 3

specified. All melting points were determined with a Yanagimoto MP-J3 micromelting point apparatus and were uncorrected. ^1H and ^{13}C NMR spectra were measured by either a Bruker AC-200P or AM-600 spectrometer using tetramethylsilane as an internal standard. ^{31}P and ^{77}Se NMR spectra were obtained with a Bruker AC-200P spectrometer using 85% H_3PO_4 and Me_2Se as an external standard, respectively. MS spectra were taken on a JEOL HX-110 or AX-500 or a Hitachi M-2500S spectrometer. IR spectra were recorded on a Horiba FT-300 spectrometer. The UV-vis spectra were obtained with a Hitachi U-3210 spectrometer.

Preparation of Phenyl Phosphorodichloridites (**5a–d**)

Compounds **5** were prepared according to the method in the literature [9b,21], but the method was slightly modified by employing the reversed addition to avoid the formation of multisubstituted compounds such as $(RO)_2PCl$ or $(RO)_3P$; thus, lithium phenoxides were added to phosphorus trichloride. A typical procedure is described for **5a**. Lithium 2,4,6-tri-*t*-butylphenoxide (10.1 mmol) was prepared from 2,4,6-*t*-butylphenol (**4a**, 2.65 g, 10.1 mmol) and a hexane solution of *n*-butyllithium (10.1 mmol) in THF (40 mL) at −78°C, then the solution was added dropwise to a THF (25 mL) solution of phosphorus trichloride (30.3 mmol) at −78°C and stirred for 10 minutes. The resulting mixture was allowed to warm to room temperature and was stirred for 2 hours. The solvents and volatile material were removed in vacuo and the residue was diluted with hexane (50 mL). Insoluble material was filtered off and the filtrate was concentrated to give 3.32 g (90% yield) of **5a**.

Phenyl phosphorodichloridites **5b–d** were similarly prepared from the corresponding phenol and phosphorus trichloride. The dichloridite **5b** was obtained in 89% yield. Because of the instability of **5c** [22] (δ_P = 202.6, $CDCl_3$) and **5d** (δ_P = 200.8, $CDCl_3$), they were immediately used for subsequent reactions without purification after usual workup.

5a: Pale yellow crystals, mp 69–72°C (from hexane, Ref. [9b] 68–72°C); ^1H NMR (200 MHz, $CDCl_3$) δ = 1.31 (9H, s, *p*-Bu^t), 1.48 (18H, s, *o*-Bu^t), and 7.31 (2H, s, arom.); $^{31}P\{^1H\}$ NMR (81 MHz, $CDCl_3$) δ = 201.9; $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$) δ = 31.7 (s, *p*-C<u>Me</u>$_3$), 32.7 (d, $^5J_{PC}$ = 6.6 Hz, *o*-C<u>Me</u>$_3$),

34.8 (d, $^6J_{PC}$ = 0.7 Hz, *p*-C$\underline{Me}_3$), 35.9 (d, $^4J_{PC}$ = 1.2 Hz, *o*-C$\underline{Me}_3$), 124.2 (d, $^4J_{PC}$ = 2.2 Hz, *m*-arom.), 141.7 (d, J_{PC} = 3.8 Hz, arom.), 146.1 (d, J_{PC} = 4.6 Hz, arom.), and 146.6 (d, J_{PC} = 2.0 Hz, arom.); IR (KBr) 1423, 1039, 1014, 980, 939, 648, 540, 486, and 413 cm^{-1}; MS (70 eV) *m/z* (rel intensity) 364 (M^+ + 2; 9), 362 (M^+; 13), 349 (M^+ − Me + 2; 14), 347 (M^+ − Me; 21), 327 (M^+ − Cl; 2), 247 (M^+ − 2Bu^t − 1; 13), and 57 (*t*-Bu^+; 100). Found: *m/z* 362.1346. Calcd for $C_{18}H_{29}OP^{35}Cl_2$: M, 362.1333.

5b: Colorless crystals, mp 43–46°C (from hexane, Ref. [9b] 44–46°C); ^{1}H NMR (200 MHz, $CDCl_3$) δ = 1.47 (18H, s, *o*-Bu^t), 2.28 (3H, t, $^4J_{HH}$ = 0.7 Hz, *p*-Me), and 7.10 (2H, bs, arom.); $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ = 202.1; $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$) δ = 21.4 (d, $^6J_{PC}$ = 0.8 Hz, *p*-Me), 32.6 (d, $^5J_{PC}$ = 6.6 Hz, *o*-C$\underline{Me}_3$), 35.6 (d, $^4J_{PC}$ = 1.2 Hz, *o*-C$\underline{Me}_3$), 127.9 (d, $^4J_{PC}$ = 2.1 Hz, *m*-arom.), 133.8 (d, J_{PC} = 2.2 Hz, arom.), 142.4 (d, J_{PC} = 3.5 Hz, arom.), and 146.2 (d, J_{PC} = 5.6 Hz, arom.); IR (neat) 1415, 1198, 1174, 1097, 999, 883, 860, 764, and 463 cm^{-1}; MS *m/z* (rel intensity) 322 (M^+ + 2; 26), 320 (M^+; 37), 307 (M^+ − Me + 2; 25), 305 (M^+ − Me; 36), 285 (M^+ − Cl; 13), and 57 (*t*-Bu^+; 100). Found: *m/z* 320.0857. Calcd for $C_{15}H_{23}OP^{35}Cl_2$: M, 320.0864.

Synthesis of Diphosphenes (**7a–d**)

A typical synthetic procedure is described for **7a**. Butyllithium (5.85 mmol, 1.69 M solution in hexane) was added dropwise to an ethereal solution (40 mL) of $ArPH_2$ (1.63 g, 5.85 mmol) at −78°C, and the resulting mixture was stirred for 5 minutes. Then, the solution was added dropwise to an ethereal solution (20 mL) of **5a** (3.27 g, 9.00 mmol) at −78°C. This mixture was allowed to warm to room temperature. Then, DBU (6.44 mmol) was added dropwise to this solution and the mixture was stirred for 3 hours at room temperature. The solvents were removed under reduced pressure. The residue was diluted with dichloromethane (60 mL). Insoluble material was removed by filtration, and the solvent was evaporated. The yellow crude product was purified by column chromatography (SiO_2/hexane:triethylamine = 100:1) to give 2.27 g (68% yield based on $ArPH_2$) of pure **7a**.

The diphosphenes **7b–d** were similarly prepared from the corresponding phenyl phosphorodichloridites and ArPHLi. Diphosphenes **7b** and **7c** were obtained in 54 and 53% yield, respectively. However, attempted isolation of **7d** was unsuccessful because of decomposition during the chromatographic treatment.

7a: Yellow needles, mp 186.5–187.5°C (hexane); ^{1}H NMR (200 MHz, $CDCl_3$) δ = 1.27 (9H, s, *p*-Bu^t), 1.31 (9H, s, *p*-Bu^t), 1.46 (18H, s, *o*-Bu^t), 1.54 (18H, s, *o*-Bu^t), 7.27 (2H, s, arom.), and 7.40 (2H, s, arom.); $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ = 409.8 and 534.1 (AB, $^1J_{PP}$ = 572.2 Hz); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$) δ = 31.3 (s, *p*-C$\underline{Me}_3$), 31.5 (s, *p*-C$\underline{Me}_3$), 32.6 (s, *o*-C$\underline{Me}_3$), 34.5 (s, *o*-C$\underline{Me}_3$), 34.6 (s, *p*-C$\underline{Me}_3$), 34.8 (s, *p*-C$\underline{Me}_3$), 36.0 (s, *o*-C$\underline{Me}_3$), 38.6 (s, *o*-C$\underline{Me}_3$), 122.0 (s, *m*-arom.), 123.2 (s, *m*-arom.), 141.6 (s, arom.), 145.1 (s, arom.), 149.6 (s, arom.), 153.6 (s, arom.), and 157.2 (d, $^2J_{PC}$ = 5.3 Hz, O-*ipso*-arom.); UV (CH_2Cl_2) 397 (sh, log ϵ 2.8) and 336 nm (3.9); IR (KBr) 1589, 1423, 1362, 1213, 1192, 1111, 868, 766, and 634 cm^{-1}; MS *m/z* (rel intensity) 569 (M^+ + 1; 10), 511 (M^+ − Bu^t; 6), 455 (M^+ − 2 Bu^t + 1; 6), 307 (ArP_2^+; 100), 251 (ArP_2^+ − Bu^t + 1; 84), and 57 (*t*-Bu^+; 58). Found: *m/z* 568.3958. Calcd for $C_{36}H_{58}OP_2$: M, 568.3963.

7b: Yellow needles, mp 171.5–172.5°C (hexane); ^{1}H NMR (200 MHz, $CDCl_3$) δ = 1.32 (9H, s, *p*-Bu^t), 1.46 (18H, s, *o*-Bu^t), 1.54 (18H, s, *o*-Bu^t), 2.27 (3H, s, *p*-Me), 7.06 (2H, s, arom.), and 7.41 (2H, s, arom.); $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ = 409.7 and 534.4 (AB, $^1J_{PP}$ = 572.3 Hz); $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$) δ = 21.2 (s, *p*-Me), 31.3 (s, *p*-C$\underline{Me}_3$), 32.4 (d, J_{PC} = 2.1 Hz, *o*-C$\underline{Me}_3$), 34.4 (d, J_{PC} = 4.0 Hz, *o*-C$\underline{Me}_3$), 34.7 (s, *p*-C$\underline{Me}_3$), 35.6 (s, *o*-C$\underline{Me}_3$), 38.6 (s, *o*-C$\underline{Me}_3$), 122.0 (s, *m*-arom.), 126.7 (s, *m*-arom.), 132.2 (s, arom.), 142.3 (s, arom.), 149.6 (s, arom.), 153.8 (s, arom.), and 157.1 (d, $^2J_{PC}$ = 9.2 Hz, O-*ipso*-arom.); UV (CH_2Cl_2) 397(sh, log ϵ 2.7) and 336 nm (3.9); IR (KBr) 1591, 1417, 1362, 1200, 1188, 1111, 860, 779, 755, and 669 cm^{-1}; MS *m/z* (rel intensity) 526 (M^+; 1), 469 (M^+ − Bu^t; 2), 413 (M^+ − 2 Bu^t + 1; 2), 307 (ArP_2^+; 49), 251 (ArP_2^+ − Bu^t + 1; 100), and 57 (*t*-Bu^+; 49). Found: *m/z* 526.3506. Calcd for $C_{33}H_{52}OP_2$: M, 526.3491. Found: C, 75.08; H, 9.84%. Calcd for $C_{33}H_{52}OP_2$: C, 75.24; H, 9.97%.

7c: Yellow needles, mp 167–168°C (hexane); ^{1}H NMR (200 MHz, $CDCl_3$) δ = 1.32 (9H, s, *p*-Bu^t), 1.47 (18H, s, *o*-Bu^t), 1.54 (18H, s, *o*-Bu^t), 6.98 (1H, t, $^3J_{HH}$ = 7.8 Hz, arom.), 7.27 (2H, d, $^3J_{HH}$ = 7.8 Hz, arom.), and 7.42 (2H, s, arom.); $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ = 410.4 and 533.2 (AB, $^1J_{PP}$ = 572.5 Hz); $^{13}C[^1H]$ NMR (150 MHz, $CDCl_3$) δ = 31.3 (s, *p*-C$\underline{Me}_3$). 32.5 (s, *o*-C$\underline{Me}_3$), 34.5 (s, *o*-C$\underline{Me}_3$), 34.8 (s, *p*-C$\underline{Me}_3$), 35.8 (s, *o*-C$\underline{Me}_3$), 38.6 (s, *o*-C$\underline{Me}_3$), 122.1 (s, *m*-arom.), 123.5 (s, *p*-arom.), 126.3 (s, *m*-arom.), 142.7 (s, arom.), 149.6 (s, arom.), 156.0 (s, arom.), and 157.2 (s, arom.); UV (CH_2Cl_2) 396 (sh, log ϵ 2.7) and 336 nm (4.0); IR (KBr) 1591, 1412, 1362, 1188, 1115, 881, 827, 800, 762, 752, and 719 cm^{-1}; MS *m/z* (rel intensity) 512 (M^+; 2), 455 (M^+ − Bu^t; 2), 399 (M^+ − 2 Bu^t + 1; 3), 307 (ArP_2^+; 54), 251 (ArP_2^+ − Bu^t + 1; 100), and 57 (*t*-Bu^+; 56). Found: *m/z* 512.3325. Calcd for $C_{32}H_{50}OP_2$: M, 512.3334. Found: C, 74.68; H, 10.13%. Calcd for $C_{32}H_{50}OP_2$: C, 74.97; H, 9.83%.

Attempted Preparation of Diphosphene ArO–P=P–OAr

Dichloridite **5a** (690 mg, 1.90 mmol) and magnesium (48.5 mg, 2.00 mmol) were stirred in THF (20 mL) at room temperature for 2 hours. The ^{31}P NMR spectrum showed that no reaction had occurred. Neither employment of ultrasonic irradiation (15

minutes of sonication) nor addition of iodine made any difference in the ^{31}P NMR spectrum, and the starting **5a** (628 mg) was recovered (91%).

Furthermore, addition of a THF (4 mL) solution of lithium naphthalenide (Li: 30.1 mg, 4.34 mmol/naphthalene: 515 mg, 4.02 mmol) to a THF (12 mL) solution of **5a** (690 mg, 1.90 mmol) at −78°C gave a complex mixture.

Synthesis of Thiadiphosphiranes (**8a–c**)

A typical synthetic procedure is described for **8a**. Diphosphene **7a** (164 mg, 0.29 mmol) and elemental sulfur (9.3 mg, 0.29 mg atom) were dissolved in pyridine (10 mL) and stirred at room temperature for 3.5 hours. Then, pyridine was evaporated under reduced pressure and the residue was diluted with hexane (20 mL). Insoluble material was filtered off and the filtrate was evaporated. After chromatography on silica gel using hexane–triethylamine (100:1), crude thiadiphosphirane **8a** was obtained. ^1H NMR analysis showed that the crude product contained a small amount of 2,4,6-tri-*t*-butylphenol (ca. 5%). The crude **8a** was then purified by washing with acetonitrile, and pure crystals of **8a** (30.2 mg) were obtained in 17% yield.

Similarly, **8b** and **8c** were prepared from elemental sulfur and the corresponding diphosphenes **7b** and **7c** in 15 and 17% yield, respectively.

8a: Colorless crystals, mp 127.5–128.5°C (MeCN); ^1H NMR (200 MHz, $CDCl_3$) δ = 1.22 (9H, s, *p*-Bu^t), 1.29 (9H, s, *p*-Bu^t), 1.48 (18H, s, *o*-Bu^t), 1.63 (18H, s, *o*-Bu^t), 7.09 (2H, d, J_{PH} = 1.7 Hz, arom.), and 7.22 (2H, s, arom.); $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ = −91.3 and 51.5 (AB, $^1J_{PP}$ = 274.5 Hz); $^{13}C\{^1H\}$ NMR (150 MHz, C_6D_6) δ = 31.1 (s, *p*-C$\underline{Me}_3$), 31.6 (s, *p*-C$\underline{Me}_3$), 33.3 (s, *o*-C$\underline{Me}_3$), 34.4 (s, *p*-$\underline{C}Me_3$), 34.5 (d, J_{PC} = 8.4 Hz, *o*-C$\underline{Me}_3$), 34.6 (s, *p*-$\underline{C}Me_3$), 36.2 (s, *o*-$\underline{C}Me_3$), 39.4 (s, *o*-$\underline{C}Me_3$), 123.8 (s, *m*-arom.), 124.0 (s, *m*-arom.), 132.9 (d, $^1J_{PC}$ = 92.7 Hz, P-*ipso*-arom.), 142.4 (s, arom.), 145.1 (s, arom.), 149.6 (s, arom.), 149.7 (s, arom.), and 156.5 (s, arom.); IR (KBr) 1471, 1423, 1394, 1363, 1184, 1103, 849, 771, and 748 cm^{-1}; MS *m/z* (rel intensity) 600 (M^+; 2), 544 (M^+ − Bu^t + 1; 29), 543 (M^+ − Bu^t; 8), 487 (M^+ − 2Bu^t + 1; 13), 355 (M^+ − Ar; 6), 339 (ArP_2S^+; 37), 276 (ArP^+; 100), 220 (ArP^+ − Bu^t + 1; 66), and 57 (*t*-Bu$^+$; 56). Found: *m/z* 600.3699. Calcd for $C_{36}H_{58}OP_2S$: M, 600.3684. Found: C, 71.81; H, 10.00%. Calcd for $C_{36}H_{58}OP_2S$: C, 71.96; H, 9.73%.

8b: Colorless crystals, mp 121–122°C (MeCN); ^1H NMR (200 MHz, $CDCl_3$) δ = 1.23 (9H, s, *p*-Bu^t), 1.47 (18H, s, *o*-Bu^t), 1.65 (18H, s, *o*-Bu^t), 2.27 (3H, s, *p*-Me), 7.02 (2H, s, arom.), and 7.11 (2H, d, J_{PH} = 1.7 Hz, arom.); $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ = −90.7 and 51.5 (AB, $^1J_{PP}$ = 274.7 Hz); $^{13}C\{^1H\}$ NMR (150 MHz, C_6D_6) δ = 21.0 (s, *p*-Me), 31.1 (s, *p*-C$\underline{Me}_3$), 33.2 (s, *o*-C$\underline{Me}_3$), 34.4$_6$ (s, *p*-$\underline{C}Me_3$), 34.4$_8$ (d, J_{PC} = 8.0 Hz, *o*-C$\underline{Me}_3$), 35.9 (s, *o*-$\underline{C}Me_3$), 39.4 (s, *o*-$\underline{C}Me_3$), 123.8 (s, *m*-arom.), 127.7 (s, *m*-arom.), 132.1 (s, arom.), 133.0 (d, $^1J_{PC}$ = 92.7 Hz, P-*ipso*-arom.), 142.9 (s, arom.), 149.6 (s, arom.), 149.7 (s, arom.), and 156.4 (s, arom.); IR (KBr) 1477, 1466, 1414, 1363, 1176, 1105, 841, and 746 cm^{-1}; MS *m/z* (rel intensity) 558 (M^+; 4), 502 (M^+ − Bu^t + 1; 34), 501 (M^+ − Bu^t; 8), 445 (M^+ − 2Bu^t + 1; 11), 339 (ArP_2S^+; 31), 313 (M^+ − Ar; 2), 307 (ArP_2^+; 6), 282 (M^+ − ArP; 68), 276 (ArP^+; 77), 220 (ArP^+ − Bu^t + 1; 100), and 57 (*t*-Bu$^+$; 82). Found: *m/z* 558.3248. Calcd for $C_{33}H_{52}OP_2S$: M, 558.3214. Found: C, 70.75; H, 9.74%. Calcd for $C_{33}H_{52}OP_2S$: C, 70.93; H, 9.38%.

8c: Colorless crystals, mp 118–119°C (MeCN); ^1H NMR (200 MHz, $CDCl_3$) δ = 1.24 (9H, s, *p*-Bu^t), 1.49 (18H, s, *o*-Bu^t), 1.65 (18H, s, *o*-Bu^t), 6.96 (1H, t, $^3J_{HH}$ = 7.8 Hz, arom.), 7.11 (2H, d, J_{PH} = 1.6 Hz, arom.), and 7.23 (2H, d, $^3J_{HH}$ = 7.8 Hz, arom.); $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ = −91.2 and 52.0 (AB, $^1J_{PP}$ = 274.4 Hz); $^{13}C\{^1H\}$ NMR (150 MHz, C_6D_6) δ = 31.1 (s, *p*-C$\underline{Me}_3$), 33.2 (s, *o*-C$\underline{Me}_3$), 34.4 (s, *p*-$\underline{C}Me_3$), 34.5 (d, J_{PC} = 8.0 Hz, *o*-C$\underline{Me}_3$), 36.0 (s, *o*-$\underline{C}Me_3$), 39.3 (s, *o*-$\underline{C}Me_3$), 123.5 (s, arom.), 123.8 (s, arom.), 127.1 (s, arom.), 132.8 (d, $^1J_{PC}$ = 92.1 Hz, P-*ipso*-arom.), 143.2 (s, arom.), 149.7 (s, arom.), 151.7 (s, arom.), and 156.5 (s, arom.); IR (KBr) 1477, 1466, 1406, 1363, 1176, 1107, 866, 825, 752, and 704 cm^{-1}; MS *m/z* (rel intensity) 544 (M^+; 3), 488 (M^+ − Bu^t + 1; 28), 487 (M^+ − Bu^t; 4), 431 (M^+ − 2Bu^t + 1; 8), 339 (ArP_2S^+; 16), 307 (ArP_2^+; 4), 276 (ArP^+; 100), 261 (ArP^+ − Me; 35), and 57 (*t*-Bu$^+$; 36). Found: *m/z* 544.3054. Calcd for $C_{32}H_{50}OP_2S$: M, 544.3058. Found: C, 70.41; H, 9.24%. Calcd for $C_{32}H_{50}OP_2S$: C, 70.55; H, 9.25%.

^{31}P NMR Study for the Reaction of Diphosphene (**7a**) *with Elemental Sulfur*

Diphosphene **7a** (35.4 mg, 62.2 μmol) and elemental sulfur (2.00 mg, 62.4 μg atom) were placed in a 5 mmϕ NMR tube, 0.5 mL of benzene-d_6 and 30 μL of triethylamine were added, and the tube was sealed. The ^{31}P NMR monitoring were carried out at room temperature. ^{31}P NMR analysis after 1 hour showed the formation of **8a** and a set of weak signals of AB pattern at δ_P 98.7 and 253.6 with J_{PP} = 730.5 Hz; however, this set of signals disappeared after ca. 5 hours.

Synthesis of Selenadiphosphiranes (**13a–c**)

A typical synthetic procedure is described for **13a**. Diphosphene **7a** (1.51 g, 2.66 mmol) was dissolved in a mixed solution of benzene (40 mL)–pyridine (20 mL), and the solution was stirred with elemental selenium (1.92 g, 24.3 mmol) at 60°C for 3 hours. Then, the solvents were removed in vacuo and the residue was diluted with hexane (60 mL). After being concentrated, the residue was separated on silica gel using hexane–triethylamine (100:1) to give a crude product, which was recrys-

tallized from acetonitrile to give 638 mg (37%) of pure **13a** as colorless crystals.

In a similar manner, selenadiphosphiranes **13b** and **13c** were prepared from the corresponding diphosphenes **7b** and **7c**. The ^{31}P NMR monitoring of reactions indicated the formation of the **13b** and **13c**. The crude products were obtained by flash column chromatography (SiO_2/hexane:triethylamine = 100:1); however, attempted further purification of **13b** and **13c** was not successful because of the partial decomposition during the chromatography.

13a: Colorless crystals, mp 107–109°C (decomp) (MeCN); ^1H NMR (200 MHz, $CDCl_3$) δ = 1.21 (9H, s, *p*-Bu^t), 1.29 (9H, s, *p*-Bu^t), 1.46 (18H, s, *o*-Bu^t), 1.60 (18H, s, *o*-Bu^t), 7.06 (2H, d, J_{PH} = 1.7 Hz, arom.), and 7.19 (2H, s, arom.); $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ = −65.2 (satellite, $^1J_{PASe}$ = 103.0 Hz) and 76.6 (satellite, $^1J_{PBSe}$ = 236.2 Hz) (AB, $^1J_{PP}$ = 289.0 Hz); $^{77}Se\{^1H\}$ NMR (38 MHz, CD_2Cl_2) δ = 27.6 (dd, $^1J_{PASe}$ = 103.3 Hz and $^1J_{PBSe}$ = 233.8 Hz); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$) δ = 31.1 (s, *p*-C$\underline{Me}_3$), 31.5 (s, *p*-C$\underline{Me}_3$), 33.1 (s, *o*-C$\underline{Me}_3$), 34.4 (s, *p*-$\underline{C}Me_3$), 34.4 (s, *p*-$\underline{C}Me_3$), 34.6 (d, J_{PC} = 8.2 Hz, *o*-C$\underline{Me}_3$), 36.0 (s, *o*-$\underline{C}Me_3$), 39.3 (s, *o*-$\underline{C}Me_3$), 123.3 (s, *m*-arom.), 123.7 (s, *m*-arom.), 128.9 (d, $^1J_{PC}$ = 91.3 Hz, P-*ipso*-arom.), 141.5 (s, arom.), 144.3 (s, arom.), 149.0 (s, arom.), 154.9 (d, J_{PC} = 2.2 Hz, arom.), and 156.2 (d, $^2J_{PC}$ = 4.4 Hz, O-*ipso*-arom.); IR (KBr) 1587, 1471, 1423, 1392, 1362, 1205, 1182, 1103, 846, 769, and 629 cm^{-1}. Found: 648.3132. Calcd for $C_{36}H_{58}OP_2Se$: M, 648.3128. Found: C, 67.05; H, 9.31%. Calcd for $C_{36}H_{58}OP_2Se$: C, 66.75; H, 9.03%.

Synthesis of 3,3-Dichloro-1-(2,4,6-tri-t-butylphenyl)-2-(2,4,6-tri-t-butylphenoxy)-1,2-diphosphirane (**16a**)

To a solution of **7a** (320 mg, 0.56 mmol) and benzyltriethylammonium chloride (63.0 mg, 0.277 mmol) in hexane (15 mL) were added 50% aqueous sodium hydroxide (15 mL) and 0.2 mL of chloroform (298 mg, 2.50 mmol). The mixture was stirred at room temperature for 3 hours. Then the organic layer was separated, washed with brine, and dried with $MgSO_4$. After evaporation of the solvent, the residue was chromatographed on silica gel using hexane as eluent to give 117 mg (32% yield) of **16a**.

16a: Colorless oil; ^1H NMR (200 MHz, C_6D_6) δ = 1.10 (9H, s, Bu^t), 1.24 (9H, s, Bu^t), 1.41 (9H, s, Bu^t), 1.64 (18H, s, *o*-Bu^t), 1.76 (9H, s, Bu^t), 7.18 (1H, bs, arom.), 7.39 (1H, bs, arom.), and 7.42 (2H, s, arom.); $^{31}P\{^1H\}$ NMR (C_6D_6) δ = −76.3 and 43.9 (AB, $^1J_{PP}$ = 159.0 Hz); MS *m/z* (rel intensity) 650 (M^+; 5), 615 (M^+ − Cl; 1), 593 (M^+ − Bu^t; 3), 389 (M^+ − ArO; 56), 333 (M^+ − ArO − Bu^t + 1; 23), and 57 (*t*-Bu$^+$; 100). Found: *m/z* 650.3346. Calcd for $C_{37}H_{58}OP_2{}^{35}Cl_2$: M, 650.3340.

The ^{31}P NMR monitoring during the reaction indicated the formation of **16a** as a major product, and AB pattern signals at δ_P 166.8 and 303.5 ppm with J_{PP} = 308.3 Hz were observed. Although these signals of AB pattern remained during the whole reaction process, even after complete consumption of the starting material, the compound giving rise to these signals decomposed during the chromatographic workup.

Attempted Conversion of Dichlorodiphosphirane (**16a**) *to 1,3-Diphosphaallene*

Dichlorodiphosphirane (**16a**; 101 mg, 155 μmol) was dissolved in THF (6 mL) and cooled at −78°C. Then, 300 μmol of *t*-butyllithium in pentane was added dropwise to the solution. The resulting mixture was allowed to warm to room temperature and stirred for 3 hours. ^{31}P NMR monitoring during the reaction showed a complicated mixture, but no evidence was observed for formation of diphosphaallene.

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