Valence Isomerism between Sterically Protected Methylenephosphine *P*-Sulfide and 1,2-Thiaphosphirane

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Reaction of (diphenylmethylene)(2,4,6-tri-*t*-butylphenyl)phosphine with elemental sulfur afforded 3,3-diphenyl-2-(2,4,6-tri-*t*-butylphenyl)-1,2-thiaphosphirane 2-sulfide via methylenephosphine *P*-sulfide. Desulfurization reaction of the thiaphosphirane 2-sulfide with tris(dimethylamino)phosphine gave 3,3-diphenyl-2-(2,4,6-tri-*t*-butylphenyl)-1,2-thiaphosphirane. Valence isomerization occurred between the methylenephosphine *P*-sulfide and the thiaphosphirane by heat or by photo-irradiation. The structures of the methylenephosphine, the methylenephosphine *P*-sulfide, and the thiaphosphirane were analyzed by X-ray crystallography.

Phosphorus-containing small ring compounds as well as low coordinated phosphorus compounds have been of interest because of their unusual bonding properties and reactivities.[1] Utilizing an extremely bulky 2,4,6-tri-*t*-butylphenyl (hereafter abbreviated to Ar) as a sterically protecting auxiliary, we have been successful in preparation of various phosphorus compounds of unusual structures such as diphosphenes **1**,[2] diphosphene monosulfides **2**,[3] and thiadiphosphiranes **3**.[4] The diphosphene monosulfide **2**, prepared by sulfurization of diphosphene **1**, was isomerized to thiadiphosphirane **3** by heat or by light (Scheme 1).[3] Similar valence isomerizations of phosphorus compounds have also been reported by Niecke et al., including the thermal conversion of amino(dimethylene)phosphorane **4a**[5] (to the corresponding aminophosphirane **4b**), methylenephosphinimidic amide **5a**[6] (to **5b**), and diazaphosphirane **6b**[7] (to **6a**).

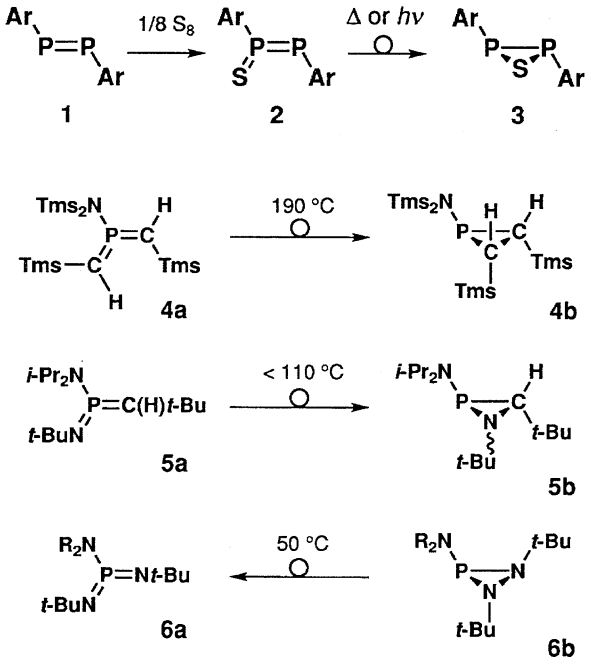
Although there have been several reports on the preparation of methylenephosphine *P*-sulfides[8] and/or thiaphosphiranes,[9] little has been known about the valence isomerism. In addition, studies on the crystal structure of methylenephosphine *P*-sulfides[8c] or thiaphosphiranes have been limited. No crystallographical study has been reported which deals with structures of both methylenephosphine *P*-sulfides and thiaphosphiranes bearing the same substituents.

Recently we have reported the preliminary results about the valence isomerism between sterically protected methylenephosphine *P*-sulfide and the corresponding thiaphosphirane derivative, including the crystal structure analysis of the latter species.[10] We report here on the structure of the other valence isomer, (diphenylmethylene)(2,4,6-tri-*t*-butylphenyl)phosphine *P*-sulfide, as well as the structure of the starting methylenephosphine with discussion on the valence isomerism in terms of temperature dependence.

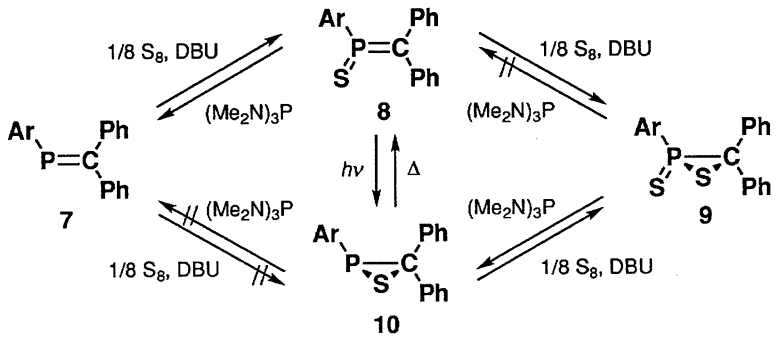
Results and Discussion

Sulfurization Reactions of (Diphenylmethylene)-(2,4,6-tri-*t*-butylphenyl)phosphine and the Related Compounds. (Diphenylmethylene)(2,4,6-tri-*t*-butylphenyl)-phosphine (**7**)[11] was prepared by the method described previously.[11a] Reaction of **7** with elemental sulfur (1.4 mol. amt. as S) in benzene in the presence of 1,8-diazabicyclo-[5.4.0]undec-7-ene (DBU) at 80 °C for 1.5 h afforded (diphenylmethylene)(2,4,6-tri-*t*-butylphenyl)phosphine *P*-sulfide (**8**) (57% yield; Scheme 2).

The compound **8** was desulfurized by tris(dimethylamino)phosphine in benzene at room temperature to give the methylenephosphine **7** (79% yield).



Scheme 1.



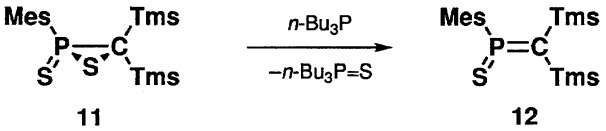
Scheme 2.

The reaction of **7** with an excess amount of sulfur at room temperature gave 1,2-thiaphosphirane 2-sulfide **9** in nearly quantitative yield (96% yield); when the reaction was performed at elevated temperature, however, the yield was low, probably because of decomposition of **9**. The formation of **9** from **8** was confirmed by the reaction with elemental sulfur (83% isolated yield; because of the instability of **9**, the isolated yield strongly depended on the conditions of the isolation process).

The compound **9** was desulfurized to thiaphosphirane **10** by some λ^3-phosphines such as tris(dimethylamino)phosphine (80% yield of **10**), tributylphosphine (55% yield), or triphenylphosphine (46% yield). The thiaphosphirane **10** was sulfurized to **9** by the reaction with elemental sulfur (5.4 mol. amt. as S) in benzene and DBU (95% yield). An attempted desulfurization of **10** with tris(dimethylamino)-phosphine resulted in the recovery of **10** (71%).

Valence Isomerism between the Methylenephosphine *P*-Sulfide and the Thiaphosphirane. Since we obtained both valence isomers **8** and **10** as described above, we have been interested in the interconversion between them. An attempted thermal isomerization of **8** (in toluene, 100 °C, 6 d) resulted in the recovery of **8** (92% after column chromatography). Heating of **8** in *m*-xylene at 130 °C in the dark for 23 h afforded many unidentified products (59% recovery of **8**) but no evidence for the formation of **10** was obtained.[12] On the contrary, heating of **10** in *m*-xylene at 130 °C in the dark for 16 h afforded **8** (32% yield) with some unidentified products. Prolonged heating under similar conditions resulted in the decomposition of **8** (see above). Heating of **10** in toluene at 100 °C in the dark for 7 d afforded **7** (8% yield), **8** (ca. 10%), and some unidentified products (28% recovery of **10**).

It should be mentioned that the desulfurization reaction of 2-mesityl-3,3-bis(trimethylsilyl)-1,2-thiaphosphirane 2-sulfide (**11**) with tributylphosphine gave methylenephosphine *P*-sulfide **12** (Scheme 3)[8c] but not the corresponding thiaphosphirane. This might indicate that the above mentioned desulfurization reaction of **9** to **10** (Scheme 2) is kinetically controlled and that **11** to **12** is thermodynamically controlled, since methylenephosphine *P*-sulfides of the type **8** appear to be more thermally stable than the corresponding thiaphosphiranes of the type **10**.



Scheme 3.

When compound **8** in benzene was irradiated with a Xe lamp (300 W) using a Toshiba UV-35 filter, **10** was obtained in 86% yield. On the other hand, irradiation of **10** in hexane in a quartz cell with a Xe lamp (500 W) using a Toshiba UV-27 filter resulted in the decomposition of **10**, giving many unidentified products. During the latter reaction, traces of **7**, **8**, and 2,4,6-tri-*t*-butylphenylthioxophosphine sulfide[13] were observed by ^{31}P NMR spectroscopy. However, it is unclear whether the formation of **8** resulted from photo-isomerization of **10** or from some other process such as desulfurization-resulfurization of **10** because the products were too complicated to be analyzed.

Molecular Structures of 7, 8, and 10. The structures of **7** and **8** were analyzed by X-ray crystallography to compare with the previously reported structure of **10**.[10] Figures 1, 2, and 3 show the molecular structures[14] for **7**, **8**, and **10** in the crystals, respectively. Some important bond lengths and angles are listed in Table 1.

The total framework of **8** resembles that of **7** except for the P=S moiety. For the compound **7**, the atoms P1, C1, C2, C8, and C14 are on the same plane within 0.007 Å. The three benzene rings (C2–C7, C8–C13, and C14–C19) are approximately perpendicular to the P=C plane with interplanar angles of 58.9°, 34.9°, and 79.5°, respectively. Similarly, the atoms P1, S1, C1, C2, C8, and C14 in **8** lie on the plane (maximum deviation, 0.036 Å). The three benzene rings (C2–C7, C8–C13, and C14–C19) of **8** are approximately perpendicular to the P=C plane with interplanar angles of 59.9°, 35.0°, and 77.7°, respectively. The phosphorus–carbon double bond for **8** [1.676(4) Å] is slightly shorter than that for **7** [1.689(3) Å]. Similarly, the bond length P1–C14 for **8** is shorter than that for **7**. A considerable difference in the bond angle is found between **7** and **8**. Probably because of the steric repulsion between the sulfur atom and the phenyl substituent [C2–C7], the compound **8** has a larger P1–C1–C2 angle [116.2(3)°] than **7** has [112.9(2)°]. Consequently, the angle P1–C1–C8 for **8** [126.2(3)°] is smaller than that for **7**

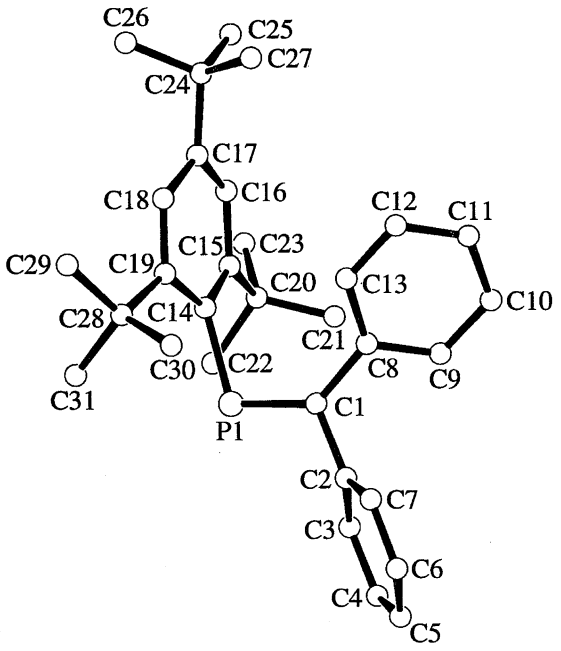


Fig. 1. Molecular structure of **7** with atom labeling scheme.

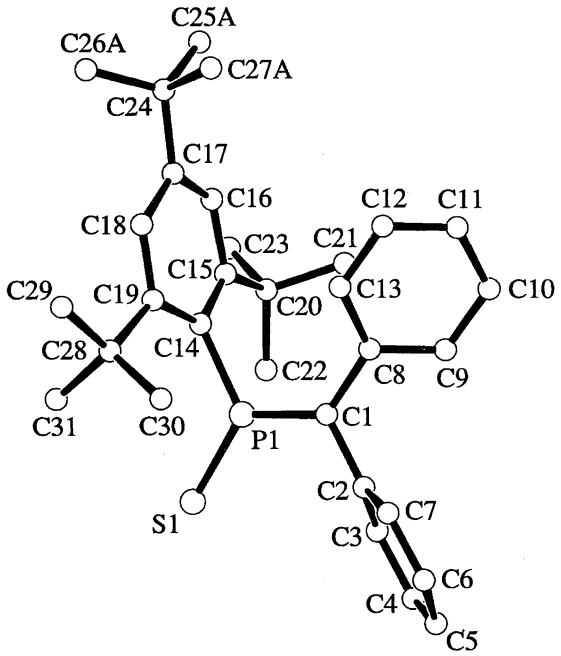


Fig. 2. Molecular structure of **8** with atom labeling scheme. The *p*-*t*-butyl group (C25–C27) is disordered and the atoms with a predominant occupancy factor (0.54) are shown for clarity.

[132.1(2)°]. The angle C1–P1–C14 in **8** [114.0(2)°] is larger than in **7** [106.2(1)°], releasing the steric repulsion between the bulky Ar group and the phenyl substituent [C8–C13].

The S1–P1–C1 angle for **10** is 54.69(7)°, while that for **8** is 123.2(2)°. The interplanar angles between the three-membered ring and the aromatic rings (C2–C7, C8–C13, and C14–C19) for **10** are 50.2°, 131.4°, and 110.2°, respectively.

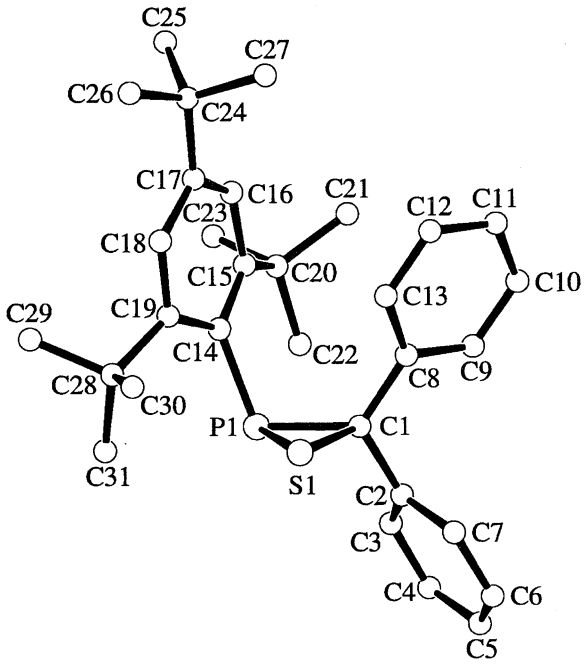


Fig. 3. Molecular structure of **10**.[10)]

Table 1. Some Important Bond Lengths (Å), Bond Angles (°), and Tilt Angles (°) of Methylenephosphine **7**, Methylenephosphine *P*-Sulfide **8**, and Thiaphosphirane **10**[a)]

	7	**8**	**10**[b)]
P1–C1	1.689(3)	1.676(4)	1.878(2)
P1–C14	1.846(3)	1.808(4)	1.855(2)
P1–S1	—	1.923(2)	2.113(1)
C1–S1	—	—	1.845(2)
C1–C2	1.492(3)	1.490(6)	1.515(3)
C1–C8	1.483(3)	1.478(6)	1.505(3)
C1–P1–C14	106.2(1)	114.0(2)	107.9(1)
P1–C1–C2	112.9(2)	116.2(3)	112.3(2)
P1–C1–C8	132.1(2)	126.2(3)	124.1(2)
C2–C1–C8	114.9(2)	117.4(3)	115.6(2)
S1–P1–C1	—	123.2(2)	54.69(7)
S1–P1–C14	—	122.8(1)	102.18(8)
P1–S1–C1	—	—	56.18(8)
S1–C1–P1	—	—	69.14(9)
S1–C1–C2	—	—	111.0(2)
S1–C1–C8	—	—	115.9(2)
Ar[c)]	79.5	77.7	—
(*E*)-Ph[d)]	58.9	59.9	—
(*Z*)-Ph[e)]	34.9	35.0	—

a) Numbers in parentheses are estimated standard deviations. b) Data taken from Ref. 10. c) Tilting angle of the aromatic ring (C14–C19) from the P=C plane (P1, C1, C2, C8, and C14). d) Tilting angle of the aromatic ring (C2–C7) from the P=C plane. e) Tilting angle of the aromatic ring (C8–C13) from the P=C plane.

Experimental

Melting points were measured on a Yanagimoto MP-J3 micro melting points apparatus and were uncorrected. NMR spectra were recorded on a Bruker AC-200P or a Bruker AM-600 spectrometer. UV spectra were measured on a Hitachi U-3210 spectrometer.

IR spectra were obtained on a Horiba FT-300 spectrometer. MS spectra were taken on either a JEOL HX-110 or a Hitachi M-2500S spectrometer. X-Ray diffraction data were collected on a Rigaku AFC-7S four-circle diffractometer. Reactions were performed under an argon atmosphere, unless otherwise specified. The starting methylenephosphine **7** was prepared by the method described previously.[11a)]

(Diphenylmethylene)(2,4,6-tri-*t*-butylphenyl)phosphine *P*-Sulfide (8): To a solution of **7** (47.6 mg, 0.108 mmol) and elemental sulfur (4.9 mg, 0.15 mg-atom) in benzene (0.4 mL) was added DBU (0.03 mmol); the resulting solution was stirred at 80 °C for 1.5 h. Removal of the solvent in vacuo, followed by column chromatographic separation (SiO_2/hexane), afforded 28.9 mg (57%) of **8** together with 4.9 mg (10% recovery) of **7**.

8: Yellow prisms, mp 119—120 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 1.36 (9H, s, *p*-*t*-Bu), 1.70 (18H, s, *o*-*t*-Bu), 6.51 (2H, dd, $^3J_{HH}$ = 7.4 Hz and $^4J_{HH}$ = 3.2 Hz, (*Z*)-*o*-Ph), 6.90 (2H, t, $^3J_{HH}$ = 7.4 Hz, (*Z*)-*m*-Ph), 6.95 (1H, dt, $^3J_{HH}$ = 7.4 Hz and $^4J_{HH}$ = 3.2 Hz, (*Z*)-*p*-Ph), 7.33 (1H, dt, $^3J_{HH}$ = 7.5 Hz and $^4J_{HH}$ = 2.3 Hz, (*E*)-*p*-Ph), 7.42 (2H, t, $^3J_{HH}$ = 7.5 Hz, (*E*)-*m*-Ph), 7.46 (2H, dd, $^3J_{HH}$ = 7.5 Hz and $^4J_{HH}$ = 2.3 Hz, (*E*)-*o*-Ph), and 7.50 (2H, d, $^4J_{PH}$ = 5.2 Hz, *m*-Ar); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ = 31.1 (s, *p*-C<u>Me</u>$_3$), 33.6 (s, *o*-C<u>Me</u>$_3$), 35.2 (d, $^5J_{PC}$ = 1.0 Hz, *p*-<u>C</u>Me$_3$), 39.5 (d, $^3J_{PC}$ = 3.0 Hz, *o*-<u>C</u>Me$_3$), 123.9 (d, $^3J_{PC}$ = 13.1 Hz, *m*-Ar), 124.0 (d, $^1J_{PC}$ = 74.9 Hz, *ipso*-Ar), 126.0 (d, $^5J_{PC}$ = 5.0 Hz, (*Z*)-*p*-Ph), 127.4 (d, $^5J_{PC}$ = 3.5 Hz, (*E*)-*p*-Ph), 127.5 (d, $^4J_{PC}$ = 2.9 Hz, (*Z*)-*m*-Ph), 128.4 (d, $^4J_{PC}$ = 1.4 Hz, (*E*)-*m*-Ph), 128.6 (d, $^3J_{PC}$ = 13.7 Hz, (*Z*)-*o*-Ph), 130.6 (d, $^3J_{PC}$ = 15.6 Hz, (*E*)-*o*-Ph), 140.2 (d, $^2J_{PC}$ = 1.2 Hz, (*Z*)-*ipso*-Ph), 140.3 (d, $^2J_{PC}$ = 2.4 Hz, (*E*)-*ipso*-Ph), 143.5 (d, $^1J_{PC}$ = 130.3 Hz, P=C), 154.2 (d, $^4J_{PC}$ = 3.5 Hz, *p*-Ar), and 154.8 (d, $^2J_{PC}$ = 5.7 Hz, *o*-Ar); ^{31}P{^{1}H} NMR (81 MHz, $CDCl_3$) δ = 154.1; UV (hexane) 225 (sh, log ϵ 4.38), 252 (4.32), and 376 nm (4.19); IR (KBr) 758, 717, 695, 675, and 596 cm^{-1}; MS (70 eV) *m/z* (rel intensity) 474 (M^+; 89), 417 ($M^+ - t$-Bu; 9), 307 ($M^+ - Ph_2C - 1$; 21), 275 ($ArP^+ - 1$;59), 220 ($ArP^+ - t$-Bu+1; 91), 199 ($Ph_2CS^+ + 1$; 90), 167 ($Ph_2C^+ + 1$; 51), and 57 (t-Bu$^+$; 100). Found: *m/z* 474.2491. Calcd for $C_{31}H_{39}PS$: M, 474.2510.

Reaction of 8 with Tris(dimethylamino)phosphine. To a solution of **8** (24.8 mg, 0.0522 mmol) in benzene (1.2 mL) was added tris(dimethylamino)phosphine (0.080 mmol) and the resulting solution was stirred at room temperature for 24 h. Removal of the solvent, followed by chromatographic separation, gave 18.3 mg (79%) of **7**.

3,3-Diphenyl-2-(2,4,6-tri-*t*-butylphenyl)-1,2-thiaphosphirane 2-Sulfide (9): To a benzene (10 mL) solution of **7** (165.0 mg, 0.374 mmol) and elemental sulfur (118.0 mg, 3.69 mg-atom) was added DBU (0.2 mmol) and the resulting solution was stirred at room temperature for 24 h. The solvent was removed under reduced pressure and the residue was separated by column chromatography (SiO_2/hexane–Et_2O) to give **9** (181.0 mg, 96% yield based on **7**). In a solution (hexane) at room temperature, compound **9** gradually decomposed.

9: Pale yellow prisms, mp ca. 50 °C (decomp); ^{1}H NMR (600 MHz, $CDCl_3$) δ = 1.32 (9H, s, *p*-*t*-Bu), 1.43 (9H, s, *o*-*t*-Bu), 1.78 (9H, s, *o*′-*t*-Bu), 6.41 (2H, d, $^3J_{HH}$ = 7.8 Hz, (*Z*)-*o*-Ph), 6.80 (2H, dd, $^4J_{PH}$ = 7.1 Hz and $^4J_{HH}$ = 2.0 Hz, *m*-Ar), 6.84 (1H, t, $^3J_{HH}$ = 7.8 Hz, (*Z*)-*m*-Ph), 6.98 (1H, t, $^3J_{HH}$ = 7.8 Hz, (*Z*)-*p*-Ph), 7.33 (1H, t, $^3J_{HH}$ = 7.5 Hz, (*E*)-*p*-Ph), 7.40 (2H, t, $^3J_{HH}$ = 7.5 Hz, (*E*)-*m*-Ph), 7.55 (1H, dd, $^4J_{PH}$ = 5.6 Hz and $^4J_{HH}$ = 2.0 Hz, *m*′-Ar), and 7.75 (2H, d, $^3J_{HH}$ = 7.5 Hz, (*E*)-*o*-Ph); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ = 31.2 (s, *p*-C<u>Me</u>$_3$), 33.1 (s, *o*-C<u>Me</u>$_3$), 34.7 (s, *p*-<u>C</u>Me$_3$), 34.9 (s, *o*′-C<u>Me</u>$_3$), 39.7 (d, $^3J_{PC}$ = 2.2 Hz, *o*-<u>C</u>Me$_3$), 41.7 (d, $^3J_{PC}$ = 3.1 Hz, *o*′-<u>C</u>Me$_3$), 56.5 (d, $^1J_{PC}$ = 24.1 Hz, PS<u>C</u>), 120.9 (d, $^3J_{PC}$ = 16.1 Hz, *m*-Ar), 126.1 (d, $^3J_{PC}$ = 14.5 Hz, *m*′-Ar), 126.3 (d, $^1J_{PC}$ = 82.3 Hz, *ipso*-Ar), 126.6 (d, $^5J_{PC}$ = 2.7 Hz, (*Z*)-*p*-Ph), 127.1 (d, $^4J_{PC}$ = 2.4 Hz, (*Z*)-*m*-Ph), 127.6 (s, (*E*)-*p*-Ph), 128.0 (s, (*E*)-*m*-Ph), 129.1 (d, $^3J_{PC}$ = 3.1 Hz, (*Z*)-*o*-Ph), 131.4 (d, $^3J_{PC}$ = 8.8 Hz, (*E*)-*o*-Ph), 138.4 (d, $^2J_{PC}$ = 5.1 Hz, (*Z*)-*ipso*-Ph), 139.3 (s, (*E*)-*ipso*-Ph), 152.7 (d, $^4J_{PC}$ = 4.1 Hz, *p*-Ar), 154.8 (d, $^2J_{PC}$ = 10.8 Hz, *o*-Ar), and 159.4 (d, $^2J_{PC}$ = 6.6 Hz, *o*′-Ar); ^{31}P{^{1}H} NMR (81 MHz, $CDCl_3$) δ=10.0; MS (70 eV) *m/z* (rel intensity) 506 (M^+; 1), 474 ($M^+ - S$; 4), 340 ($ArPS_2^+$; 4), 284 ($ArPS_2^+ - t$-Bu+1; 56), 198 (Ph_2CS^+; 90), 165 ($Ph_2C^+ - 1$; 100), 121 ($PhCS^+$; 92), and 57 (t-Bu$^+$; 97). Found: *m/z* 506.2243. Calcd for $C_{31}H_{39}PS_2$: M, 506.2231.

Reaction of 8 with Sulfur. A mixture of the methylenephosphine *P*-sulfide **8** (117.0 mg, 0.246 mmol) and elemental sulfur (30.1 mg, 0.94 mg-atom) was dissolved in 20 mL of benzene and DBU (0.3 μmol) was added. The resulting solution was stirred at room temperature for 38 h and then the solvent was removed in vacuo. The ^{31}P NMR spectrum of the residue indicated the existence of small amount of the starting **8**, then benzene (20 mL), sulfur (115.6 mg, 3.6 mg-atom), and DBU (0.13 μmol) were added again. After being stirred for 18 h, the solution was worked up to give 103.1 mg (83%) of **9**.

3,3-Diphenyl-2-(2,4,6-tri-*t*-butylphenyl)-1,2-thiaphosphirane (10): To a solution of **9** (116.0 mg, 0.229 mmol) in benzene (5 mL) was added tris(dimethylamino)phosphine (5.5 mmol) and the resulting solution was stirred at room temperature for 3 h. Then the solvent was removed in vacuo and the residue was separated by column chromatography (SiO_2/hexane–Et_2O) to give **10** (86.7 mg, 80%) after recrystallization from methanol. The compound **10** was also obtained by desulfurization reaction of **9** with tributylphosphine (55% yield) or triphenylphosphine (46% yield) under similar conditions.

10: Pale yellow plates, mp 144.5—145.0 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 1.24 (9H, s, *o*-*t*-Bu), 1.27 (9H, s, *p*-*t*-Bu), 1.66 (9H, s, *o*′-*t*-Bu), 6.42 (2H, d, $^3J_{HH}$ = 7.5 Hz, (*Z*)-*o*-Ph), 6.66 (1H, s, *m*-Ar), 6.78 (2H, dd, $^3J_{HH}$ = 7.5 Hz, (*Z*)-*m*-Ph), 6.91 (1H, t, $^3J_{HH}$ = 7.5 Hz, (*Z*)-*p*-Ph), 7.26 (1H, t, $^3J_{HH}$ = 7.4 Hz, (*E*)-*p*-Ph), 7.32 (1H, s, *m*′-Ar), 7.32 (2H, dd, $^3J_{HH}$ = 7.4 Hz, (*E*)-*m*-Ph), and 7.52 (2H, d, $^3J_{HH}$ = 7.4 Hz, (*E*)-*o*-Ph); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ = 31.4 (s, *p*-C<u>Me</u>$_3$), 33.1 (d, $^4J_{PC}$ = 7.1 Hz, *o*-C<u>Me</u>$_3$), 34.0 (d, $^5J_{PC}$ = 6.5 Hz, *p*-<u>C</u>Me$_3$), 34.5 (d, $^4J_{PC}$ = 12.4 Hz, *o*′-C<u>Me</u>$_3$), 38.8 (s, *o*′-<u>C</u>Me$_3$), 40.0 (s, *o*-<u>C</u>Me$_3$), 61.9 (d, $^1J_{PC}$ = 57.1 Hz, PS<u>C</u>), 121.1 (s, *m*′-Ar), 123.9 (s, *m*-Ar), 125.6 (s, (*Z*)-*p*-Ph), 126.7 (s, (*Z*)-*m*-Ph), 127.1 (s, (*E*)-*p*-Ph), 128.5 (s, (*E*)-*m*-Ph), 129.0 (s, (*Z*)-*o*-Ph), 130.3 (d, $^3J_{PC}$ = 12.2 Hz, (*E*)-*o*-Ph), 130.5 (d, $^1J_{PC}$ = 89.8 Hz, *ipso*-Ar), 140.3 (s, (*Z*)-*ipso*-Ph), 145.7 (d, $^2J_{PC}$ = 13.5 Hz, (*E*)-*ipso*-Ph), 149.5 (s, *p*-Ar), 156.7 (d, $^2J_{PC}$ = 5.9 Hz, *o*′-Ar), and 160.2 (d, $^5J_{PC}$ = 5.9 Hz, *o*-Ar); ^{31}P{^{1}H} NMR (81 MHz, $CDCl_3$) δ = −34.9; UV (hexane) 234 (sh, log ϵ 4.4) and 281 nm (sh, 3.9); IR (KBr) 1589, 1471, 1442, 1392, 1362, 756, and 696 cm^{-1}; MS (70 eV) *m/z* (rel intensity) 474 (M^+; 27), 442 ($M^+ - S$; 10), 275 ($ArP^+ - 1$; 83), 199 ($Ph_2CS^+ + 1$; 43), and 57 (t-Bu$^+$; 100). Found: *m/z* 474.2528. Calcd for $C_{31}H_{39}PS$: M, 474.2510.

Reaction of 10 with Sulfur. A mixture of **10** (27.7 mg, 0.0584 mmol) and elemental sulfur (10.2 mg, 0.318 mg-atom) was dissolved in 1.7 mL of benzene, then 0.01 mmol of DBU was added. The resulting solution was stirred at room temperature for 18 h and worked up to give 28.2 mg (95%) of **9**.

Attempted Desulfurization Reaction of 10 with Tris(dimethylamino)phosphine. A benzene (0.5 mL) solution of **10** (11.4 mg, 0.024 mmol) and tris(dimethylamino)phosphine (0.421 mmol) was stirred at room temperature for 67 h. ^{31}P NMR spectrum of the solution showed no significant change and 8.3 mg (71%) of **10** was

recovered after column chromatography.

Attempted Thermal Isomerization of 8. A solution of **8** (38.6 mg, 0.0813 mmol) in toluene-d_8 (0.4 mL) was heated at 100 °C for 135 h; no significant change was observed in the ^{1}H and ^{31}P NMR spectra of the solution. After silica gel column chromatography, 35.6 mg (92%) of **8** was recovered. When a solution of **8** (5.9 mg, 0.012 mmol) in *m*-xylene (3 mL) was heated at 130 °C in the dark for 23 h, **8** (3.5 mg) was recovered (59%). In the latter reaction, trace amounts of unidentified products were observed by ^{31}P NMR spectroscopy but **10** was not detected during the reaction.

Thermal Isomerization of 10. A solution of **10** (30.5 mg, 0.0643 mmol) in *m*-xylene (5 mL) was heated at 130 °C for 16 h. Removal of the solvent, followed by column chromatographic separation (SiO_2/hexane), gave **8** (9.7 mg, 32%).

Photoisomerization of 8. A solution of **8** (19.4 mg, 0.0409 mmol) in benzene-d_6 (0.4 mL) in a Pyrex tube was irradiated with a 300-W Xe lamp using a Toshiba UV-35 filter for 1 h and the solvent was evaporated. Column chromatographic separation of the residue afforded a mixture (17.0 mg) of **10** (86% yield, determined by ^{1}H NMR) and **7** (2% yield).

X-Ray Crystal Structure Determination of 7. $C_{31}H_{39}P$, $M_r = 442.62$. Monoclinic, space group $P2_1/c$, $a = 14.265(2)$, $b = 10.838(2)$, $c = 18.471(1)$ Å; $\beta = 106.830(8)°$; $V = 2733.4(5)$ Å^3, $Z = 4$, $\rho = 1.075$ g cm^{-3}, $\mu = 1.16$ cm^{-1}; 5087 unique reflections with $2\theta \leq 50.0°$ were recorded on a four-circle diffractometer (Mo $K\alpha$ radiation, graphite monochrometer). Of these, 3443 with $I > 3\sigma(I)$ were judged as observed. The structure was solved with SHELXS86.[15] Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. $R = 0.050$, $R_w = 0.047$.

X-Ray Crystal Structure Determination of 8. $C_{31}H_{39}PS$, M_r=474.68. Monoclinic, space group $P2_1/n$, $a = 9.894(3)$, $b = 21.684(3)$, $c = 13.452(3)$ Å; $\beta = 99.50(2)°$; $V = 2846(1)$ Å^3, $Z = 4$, $\rho = 1.108$ g cm^{-3}, $\mu = 1.86$ cm^{-1}; 5175 unique reflections with $2\theta \leq 50.0°$ were recorded on a four-circle diffractometer (Mo $K\alpha$ radiation, graphite monochrometer). Of these, 3477 with $I > 3\sigma(I)$ were judged as observed. The structure was solved with SHELXS86. Methyl carbons of the *p*-*t*-butyl group are disordered. Each of these was resolved into two positions from a difference Fourier map and the occupancy factors were refined to be 0.54 and 0.46. Non-hydrogen atoms except the disordered carbon atoms were refined anisotropically. Hydrogen atoms were included but not refined. $R = 0.070$, $R_w = 0.087$.

Further details of the crystal structure investigation for **7** and **8** are available on request from the Director of the Cambridge Crystallographic Data Centre, 12 Union Road, GB-Cambridge CB2 1EZ, (U.K.). The complete *Fo*-*Fc* data have been deposited as Document No. 68070 at the Office of the Editor of Bull. Chem. Soc. Jpn.

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