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Preparation and X-Ray Structure Analysis of 3,3-Diphenyl-2-(2,4,6-tri-*t*-butylphenyl)-1,2-thiaphosphirane

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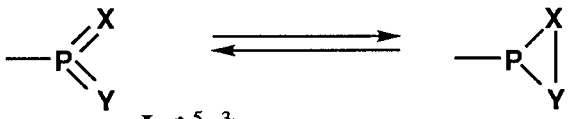
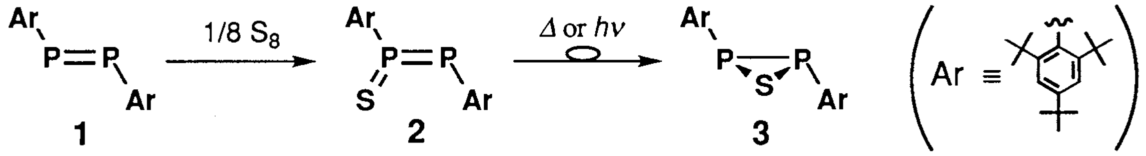
Reaction of low coordinated 2,2-diphenyl-1-(2,4,6-tri-*t*-butylphenyl)phosphaethene with elemental sulfur afforded the corresponding 1,2-thiaphosphirane 2-sulfide **6** via methylene(thioxo)phosphorane **5**. Desulfurization reaction of **6** gave the corresponding thiaphosphirane **7** and the structure was analyzed by X-ray crystallography. Valence isomerism between **5** and **7** by heat or light was studied.

Physicochemical properties of organic and inorganic small ring compounds are of current interest. Phosphorus-containing three membered ring have attracted special interest because of their valence isomerism between $\lambda^5\sigma^3$ phosphoranes (**I**) and $\lambda^3\sigma^3$ phosphiranes (**II**), although the number of well investigated examples have been limited. Niecke et al. reported the thermal conversion of imino(methylene)phosphorane (**I**, X=CRR', Y=NR") and dimethylenephosphorane (**I**, X=Y=CRR') to the corresponding azaphosphirane and phosphirane of type **II**.$^{1)}$ Generation of **I** from **II** has also been reported in the case of X=Y=NR.$^{2)}$



I ($\lambda^5\sigma^3$) **II** ($\lambda^3\sigma^3$)

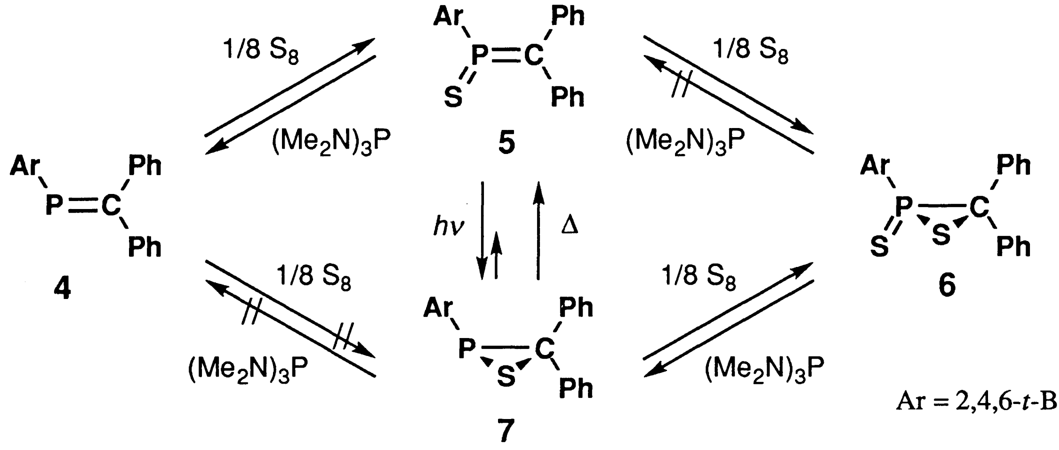
We have previously reported the isomerization of **I** to **II** in the sterically protected diphosphene systems. Thus, sulfurization reaction of 1,2-bis(2,4,6-tri-*t*-butylphenyl)diphosphene (**1**)$^{3)}$ gave diphosphene *P*-sulfide **2**, which was isomerized to thiadiphosphirane **3** by heat or by light.$^{4)}$



1 **2** **3**

Although there have been several reports on the preparations of methylene(thioxo)phosphoranes (type **I**, X=S, Y=CRR')$^{5)}$ and/or thiaphosphiranes (type **II**, X=S, Y=CRR'),$^{6)}$ to the best of our knowledge, there has been no report on the valence isomerism between them. We report here the photo-isomerization of $\lambda^5\sigma^3$ methylene(thioxo)phosphorane to $\lambda^3\sigma^3$ thiaphosphirane as well as the first X-ray crystal structure analysis of the latter compound.

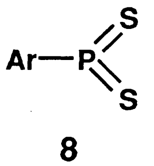
2,2-Diphenyl-1-(2,4,6-tri-*t*-butylphenyl)-1-phosphaethene (**4**)$^{7)}$ was prepared by the method described previously.$^{7a)}$ Reaction of **4** (47.6 mg, 0.108 mmol) with elemental sulfur (4.9 mg, 0.15 mg-atom) in benzene (0.4 mL) in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU; 0.03 mmol) at 80 °C for 1.5 h afforded 28.9 mg (57% yield) of methylene(thioxo)phosphorane **5** together with 4.9 mg (10% recovery) of the starting **4** after column chromatographic separation (SiO_2 / hexane). The compound **5** (0.0522 mmol) in benzene was desulfurized with tris(dimethylamino)phosphine (0.0798 mmol) at room temperature for 24 h to give **4** in 79% yield.



$Ar = 2,4,6\text{-}t\text{-}Bu_3C_6H_2$

The reaction of **4** (165.0 mg, 0.374 mmol) with an excess amount of elemental sulfur (118.0 mg, 3.69 mg-atom) in benzene (10 mL) in the presence of DBU (0.2 mmol) at room temperature for 24 h afforded 181.0 mg (96%) of 1,2-thiaphosphirane 2-sulfide **6**. In this reaction, intermediary formation of **5** was observed by ^{31}P NMR spectroscopy. **5**: Yellow prisms, mp 119–120 °C; ^{1}H NMR (200 MHz, $CDCl_3$) $\delta = 1.34$ (9H, s, *p*-Bu^t), 1.68 (18H, s, *o*-Bu^t), 6.4–6.6 (2H, m, Ph), 6.8–7.0 (3H, m, Ph), 7.2–7.5 (5H, m, Ph), and 7.47 (2H, d, $^4J_{PH} = 5.2$ Hz, *m*-Ar); $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$) $\delta = 143.5$ (d, $^1J_{PC} = 130.5$ Hz, P(S)=$\underline{C}$); $^{31}P\{^1H\}$ NMR (81 MHz, $CDCl_3$) $\delta = 154.1$; 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^+–Bu^t+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. **6**: Pale yellow prisms, mp >50 °C (decomp); ^{1}H NMR (600 MHz, $CDCl_3$) $\delta = 1.32$ (9H, s, *p*-Bu^t), 1.43 (9H, s, *o*-Bu^t), 1.78 (9H, s, *o*'-Bu^t), and 6.4–7.8 (12H, m, *m*-Ar and Ph); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$) $\delta = 56.5$ (d, $^1J_{PC} = 24.1$ Hz, PS$\underline{C}$); $^{31}P\{^1H\}$ NMR ($CDCl_3$) $\delta = 10.0$; MS *m/z* (rel intensity) 506 (M^+; 1), 474 (M^+–S; 4), 340 ($ArPS_2^+$; 4), 284 ($ArPS_2^+$–Bu^t; 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.

The compound **6** was not so stable that it slowly decomposed in the solution even at room temperature. In C_6D_6 (0.5 mL) at 65 °C (15 days), **6** (0.158 mmol) decomposed to λ^3-thiaphosphirane **7**, dithioxophosphorane **8** ($\delta_P = 297.0$), and thiobenzophenone. The formation of thiobenzophenone was confirmed by following the reaction with UV-vis spectroscopy (λ_{max} 618 nm). During column chromatography (SiO_2 / hexane - Et_2O), however, thiobenzophenone changed to benzophenone, thus thiaphosphirane **7** (0.054 mmol), benzophenone (0.033 mmol), and sulfur (0.092 mmol) were isolated. Thermal extrusion of intermediary carbene (Ph_2C:) or thioxophosphine (ArP=S) may be involved in this reaction and the mechanistic study is in progress.



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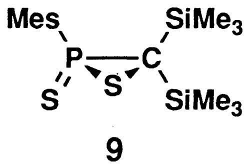

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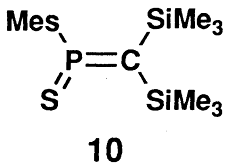

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$Ar = 2,4,6\text{-}t\text{-}Bu_3C_6H_2$

$Mes = 2,4,6\text{-}Me_3C_6H_2$

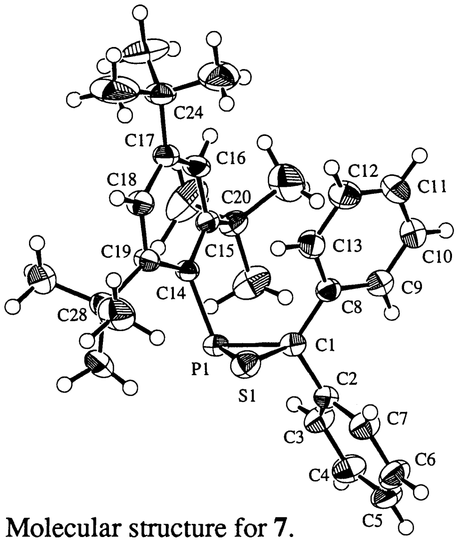

Fig. 1. Molecular structure for **7**.

Table 1. Important Bond Lengths and Angles of **7**

Bond length / Å		Bond angle / °	
P1–S1	2.113(1)	P1–S1–C1	56.18(8)
P1–C1	1.878(2)	S1–P1–C1	54.69(7)
S1–C1	1.845(2)	S1–C1–P1	69.14(9)
P1–C14	1.855(2)	C1–P1–C14	107.9(1)
C1–C2	1.515(3)	P1–C1–C2	112.3(2)
C1–C8	1.505(3)	P1–C1–C8	124.1(2)
		C2–C1–C8	115.6(2)
		S1-P1-C14	102.18(8)
		S1–C1–C2	111.0(2)
		S1–C1–C8	115.9(2)

Desulfurization reaction of **6** (116.0 mg, 0.229 mmol) with excess tris(dimethylamino)phosphine (5.5 mmol) in benzene (5 mL) at room temperature for 3 h gave the corresponding thiaphosphirane **7** (86.7 mg, 80% yield) after chromatographic separation (SiO_2 / hexane - Et_2O) and recrystallization from methanol. **7**: Colorless plates, mp 144.5 – 145.0 °C (MeOH); ^1H NMR (600 MHz, $CDCl_3$) $\delta = 1.24$ (9H, s, *o*-Bu^t), 1.27 (9H, s, *p*-Bu^t), 1.66 (9H, s, *o*'-Bu^t), 6.42–7.52 (10H, m, Ph), 6.66 (1H, s, *m*-Ar), and 7.32 (1H, s, *m*'-Ar); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$) $\delta = 61.9$ (d, $^1J_{PC} = 57.1$ Hz, PS$\underline{C}$); $^{31}P\{^1H\}$ NMR ($CDCl_3$) $\delta = -34.9$; UV (hexane) 234 (sh, log ε 4.44) and 281 nm (sh, 3.88); IR (KBr) 1589, 1471, 1442, 1392, 1362, 756, and 696 cm^{-1}; MS *m/z* (rel intensity) 474 (M^+; 27), 442 (M^+–S; 10), 275 (ArP^+–1; 83), 199 ($SCPh_2{}^+$+1; 43), and 57 (*t*-Bu^+; 100). Found: *m/z* 474.2528. Calcd for $C_{31}H_{39}PS$: M, 474.2510.

The compound **7** was also obtained by desulfurization reaction of **6** with tributylphosphine (55% yield) or triphenylphosphine (46% yield) under similar conditions. It should be mentioned that this desulfurization reaction of **6** to **7** proceeded in contrast to the reported results on the desulfurization reaction of 2-mesityl-3,3-bis(trimethylsilyl)-1,2-thiaphosphirane 2-sulfide (**9**) with tributylphosphine giving the corresponding methylene(thioxo)phosphorane **10**.[5c)] Reaction of **7** (0.0584 mmol) with sulfur (0.318 mg-atom) in benzene in the presence of DBU (0.01 mmol) at room temperature for 18 h reproduced **6** in 95% yield after chromatography. Attempted desulfurization reaction of **7** with $(Me_2N)_3P$ at room temperature for 67 h resulted in the recovery of **7** (71% after column chromatography).

The structure of **7** was unambiguously determined by the X-ray crystallography.[8)] Figure 1 depicts an ORTEP[9)] drawing of the molecular structure for **7** in the crystals (ellipsoids drawn at 50% probability level). Some important bond lengths and angles for **7** are listed in Table 1. As for the three membered ring, the bond lengths P1–C1 and P1–S1 for **6** (1.878(2) and 2.113(1) Å, respectively) is longer than those for **9**[5c)] (1.795(7) and 2.049(3) Å, respectively), although the bond length S1–C1 for **7** (1.845(2) Å) is shorter than that for **9** (1.918(8) Å). The interplanar angles between the thiaphosphirane ring and the three aromatic rings (i.e. C2–C7, C8–C13, and C14–C19) are 50.2°, 131.4°, and 110.2°, respectively.

Since we obtained the both valence isomers **5** and **7** as described above, we then investigated the interconversion between them. Heating of **5** in *m*-xylene at 130 °C in the dark for 3 days afforded a mixture of unidentified products but evidence for formation of **7** was not obtained.[10)] However, heating of **7** in *m*-xylene at 130 °C in the dark for 3 days afforded **5** (17% yield) together with some unidentified products. Irradiation of

5 (0.02 mmol) in C_6D_6 (0.4 mL) in a Pyrex tube with a mercury lamp (medium pressure, 100 W) at 10 °C for 1.5 h gave **7** as a major product along with some by-products (observed by ^{31}P NMR spectroscopy). After flash chromatography and recrystallization, **7** was obtained in 35% yield. In addition, formation of **5** was observed, along with some by-products, by irradiation of **7** in hexane in a quartz tube for 45 min (**5** : **7** = 1 : 20, by ^{31}P NMR spectroscopy).

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8) Crystal data of **7**: Recrystallized from methanol. $C_{31}H_{39}PS$, $M_r = 474.68$. Monoclinic, space group $C2/c$, $a = 28.631(4)$, $b = 10.718(3)$, $c = 19.696(3)$ Å; $\beta = 112.242(8)°$; $V = 5594(1)$ Å^3, $Z = 8$, $\rho = 1.127$ gcm^{-3}, $\mu = 1.89$ cm^{-1}; 5227 unique reflections with $2\theta \le 50.0°$ were recorded on a four-circle diffractometer (MoKα radiation, graphite monochrometer). Of these, 3564 with $I > 3\sigma(I)$ were judged as observed. The structure was solved with SHELXS86.[11] The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined isotropically. $R = 0.041$, $R_w = 0.037$. Further details of the crystal structure investigation are available on request from the Director of the Cambridge Crystallographic Data Centre, 12 Union Road, GB-Cambridge CB2 1EZ (UK).

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