Heteroatom Chemistry
Volume 1, Number 3, 1990

X-Ray Structure of 3-Diphenylmethylene-2-(2,4,6-tri-*t*-butylphenyl)thiaphosphirane 2-Sulfide: The First Thiaphosphirane with *exo*-Methylene

Ken Hirotsu* and Akihiro Okamoto
Department of Chemistry, Faculty of Science, Osaka City University, Sumiyoshi-ku, Osaka 558, Japan
Kozo Toyota and Masaaki Yoshifuji*
Department of Chemistry, Faculty of Science, Tohoku University, Aoba, Sendai 980, Japan

Received 12 December 1989.

ABSTRACT

The title compound was prepared by sulfurization of a 1-phosphaallene and its x-ray structure analysis showed the following notable features of the thiaphosphirane ring: P-S = 2.101(2), P-C = 1.770(5) and S-C = *1.767(5) Å (remarkably short), and ∠SPC = 53.5(2), ∠PSC = 53.6(2) and ∠PCS = 72.9(2)°.*

Phosphorus-containing small ring compounds as well as pπ-bonded P^{III} and P^{V} compounds are of current interest, particularly with respect to their bonding properties and reactivities. Kinetic stabilization with bulky substituents has been applied in many attempts to isolate unstable compounds. Bulky groups are also known to stabilize three-membered heterocyclic compounds with an exocyclic double bond, which are of special interest in view of their ring strain and reactivities [1]. By introducing an extremely bulky 2,4,6-tri-*t*-butylphenyl group into a molecule as a protecting group, we have been successful in the preparation and characterization of some P=C double-bonded compounds, such as *E*- and *Z*-2-phenyl-1-(2,4,6,tri-*t*-butylphenyl)phosphaethylenes [2], 3-phenyl-1-(2,4,6-tri-t-butylphenyl)-3-aza-1-phosphaallene[3], 1,3-bis(2,4,6-tri-*t*-butylphenyl)-1,3-diphosphaallene [4, 5], and 3,3-diphenyl-1-(2,4,6-tri-*t*-butylphenyl)-1-phosphaallene (**1**) [3, 6]. We report here the x-ray crystal structure and some spectroscopic properties of 3-diphenylmethylene-2-(2,4,6-tri-*t*-butylphenyl)thiaphosphirane 2-sulfide (**3**), the first thiaphosphirane with an *exo*-methylene group.

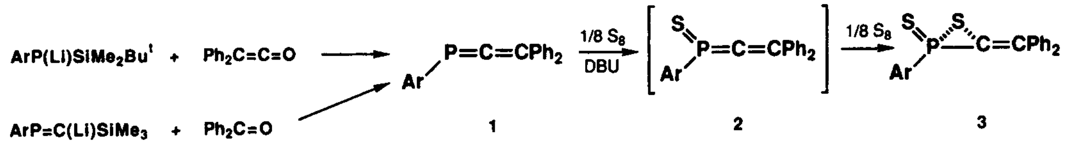
RESULTS AND DISCUSSION

The starting material, 3,3-diphenyl-1-(2,4,6-tri-*t*-butylphenyl)-1-phosphaallene (**1**) was prepared by either reaction of a lithium silylphosphide with diphenylketene [3] or reaction of a 1-silyl-2-phosphaethenyl-lithium with benzophenone [6] (Scheme 1). The title compound, 3-diphenylmethylene-2-(2,4,6-tri-*t*-butylphenyl)thiaphosphirane 2-sulfide (**3**) was prepared by sulfurization of **1** by the method previously described by ourselves [7]. When the ^{31}P nuclear magnetic resonance (NMR) spectrum was taken during the reaction, a peak appeared at δ_P 79 and indicated the initial formation of the 1-phosphaallene 1-sulfide **2** as an intermediate, similar to the results of sulfurization reactions of phosphorus double-bonded compounds such as phosphaalkenes and diphosphenes [8–10].

---

* To whom correspondence should be addressed.

1042-7163/90/$3.50 + .25



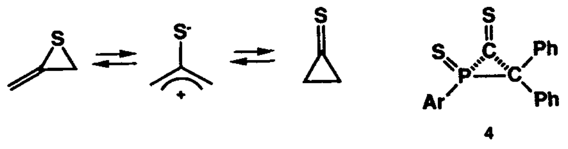
Ar = 2,4,6-$Bu^t{}_3C_6H_2$; DBU = 1,8-diazabicyclo[5.4.0]undec-7-ene

SCHEME 1

Compound **3** is a phosphorus analogue of allene episulfide, which is thermodynamically more stable than its valence isomer, cyclopropanethione [11] (Scheme 2). The observed upfield chemical shift at δ_P -18.9 for **3** is characteristic of phosphorus-containing small ring compounds, and the ^{13}C NMR spectrum showed two olefinic carbons at δ 141.1 (d, $^2J_{PC}$ = 16.2 Hz, PC=*C*) and 125.4 (d, $^1J_{PC}$ = 64.3 Hz, P*C*=C), both of which are coupled with the phosphorus atom to give two sets of doublets. No ^{13}C NMR peak was detected lower than those of the aromatic region. Thus, a valence isomeric structure phosphirane 1,2-disulfide **4** is excluded, because thiocarbonyl carbons in general have δ 180–210 ppm. It should be noted here that the ^1H NMR spectrum of **3** showed two signals due to *o*-*t*-butyl groups, indicating that the molecule is suffering hindered rotation of the 2,4,6-tri-*t*-butylphenyl ring around the P-C bond surrounded by the other two phenyl rings.

The structure of **3** was unambiguously established by x-ray crystallographic analysis. Figure 1 shows the ORTEP [12] drawing of the molecular structure for **3**. The P, S(1), C(1), C(2), C(21), and C(27) are coplanar within 0.127(6) Å. The S(2) and C(3) atoms are above and below this plane by 1.546(4) and 1.523(5) Å, respectively. The tri-*t*-butylphenyl ring [C(3)-C(8)] makes an angle of 70.7° with this plane. Other phenyl rings at C(2), [C(21)-C(26)], and [C(27)-C(32)] make angles of 46.4° and 44.0° with the plane, respectively. The interplanar angle between the planes [P, S(1), C(1)] and [P, S(2), C(3)] is 79.4°, and that between the planes [P, S(2), C(3)] and [C(3)-C(8)] is 78.8°. The P=S bond length for **3** (1.923(2) Å) is very similar to that for 2-mesityl-3,3-bis(trimethylsilyl)thiaphosphirane 2-sulfide (**5**) (1.932(3) Å) reported by Caira et al. [9]. The P-S(1) bond length of the thiaphosphirane ring for **3** (2.101(2) Å) is slightly longer than that for **5** (2.049(3) Å) and very similar to that for *E*-2,3-bis(2,4,6-tri-*t*-butylphenyl)-1,2,3-thiadiphosphirane(**6**) (2.103(3) Å) [13]. However, the S(1)-C(1) bond length of the ring (1.767(5) Å) for **3** is considerably shorter than the corresponding bond length for **5** (1.918(8) Å). The P-C(1) bond length of the ring (1.770(5) Å) is similar to that for **5** (1.795(7) Å). The *exo*-cyclic double bond [C(1)-C(2), 1.340(7) Å] is slightly longer than that for the 1-phosphaallene **1** (1.327(5) Å) [7, 14]. The benzene ring of the 2,4,6-tri-*t*-butylphenyl group is distorted to an envelope form and atoms C(4)-C(8) are coplanar. Some important bond lengths and angles for **3** are listed in Table 1. The positional parameters are listed in Table 2.

SCHEME 2



EXPERIMENTAL

The ^1H and ^{13}C NMR spectra were recorded on JEOL FX-90Q and Varian XL-200 spectrometers at ambient temperature using tetramethylsilane as an internal standard. The ^{31}P NMR spectra were measured with a JEOL FX-90Q spectrometer (36.2 MHz) using 85% phosphoric acid as an external standard at 30°C. The chemical shifts are expressed in parts per million downfield from the standard. The infrared spectra were collected with a Horiba FT-300 spectrometer. The ultraviolet spectra were

FIGURE 1 X-ray structure of **3**.

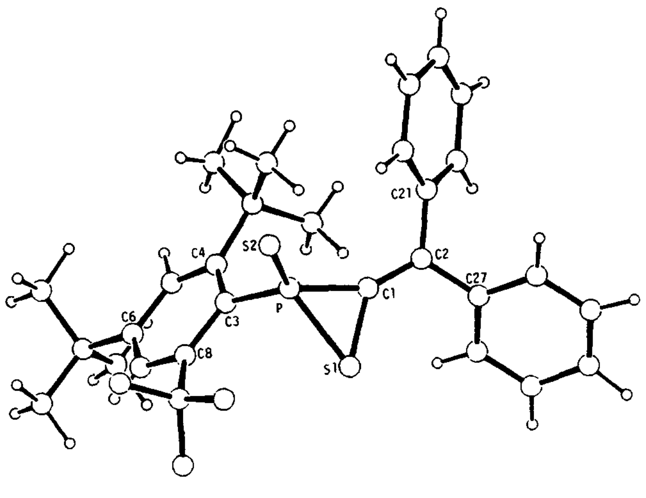


TABLE 1 Some Important Bond Lengths (Å) and Angles (°) for **3**[a]

Atom	*Bond Length* (Å)	*Atom*	*Bond Angle* (°)
P-S(1)	2.101(2)	∠S(1)-P-C(1)	53.5(2)
P-C(1)	1.770(5)	∠P-C(1)-S(1)	72.9(2)
S(1)-C(1)	1.767(5)	∠P-S(1)-C(1)	53.6(2)
P-S(2)	1.923(2)	∠P-C(1)-C(2)	151.1(4)
P-C(3)	1.833(5)	∠S(1)-C(1)-C(2)	133.2(4)
C(1)-C(2)	1.340(7)	∠S(1)-P-C(3)	106.1(1)
C(2)-C(21)	1.476(7)	∠C(1)-P-C(3)	118.8(2)
C(2)-C(27)	1.482(7)	∠S(1)-P-S(2)	123.8(1)
		∠S(2)-P-C(1)	119.7(2)
		∠S(2)-P-C(3)	118.1(2)
		∠C(1)-C(2)-C(21)	123.2(4)
		∠C(1)-C(2)-C(27)	120.1(4)
		∠C(21)-C(2)-C(27)	116.6(4)

---

[a] Standard deviations of the least significant figures are given in parentheses.

TABLE 2 Fractional Coordinates and Equivalent Isotropic Displacement Coefficients (Å^2) for **3**

	X[a]	*Y*[a]	*Z*[a]	*U*(eq)[a,b]
P	0.6709(1)	0.2411(1)	0.3956(1)	0.0377(4)
S1	0.6286(1)	0.0570(1)	0.3528(1)	0.0442(4)
S2	0.6144(1)	0.3958(1)	0.3721(1)	0.061(1)
C1	0.6549(2)	0.1197(5)	0.4693(3)	0.042(2)
C2	0.6428(2)	0.0827(4)	0.5486(3)	0.038(2)
C3	0.7579(2)	0.2455(4)	0.3773(3)	0.035(1)
C4	0.8229(2)	0.2561(4)	0.4532(3)	0.040(2)
C5	0.8862(2)	0.2455(5)	0.4347(3)	0.047(2)
C6	0.8901(2)	0.2315(4)	0.3444(3)	0.040(2)
C7	0.8264(2)	0.2283(5)	0.2720(3)	0.043(2)
C8	0.7586(2)	0.2350(4)	0.2813(3)	0.038(2)
C9	0.8325(3)	0.2772(6)	0.5609(3)	0.051(2)
C10	0.8305(3)	0.1470(7)	0.6061(4)	0.072(3)
C11	0.7771(3)	0.3682(6)	0.5748(4)	0.064(2)
C12	0.9054(4)	0.3371(9)	0.6144(5)	0.097(3)
C13	0.9629(2)	0.2246(5)	0.3312(3)	0.046(2)
C14	0.9574(3)	0.2189(6)	0.2271(4)	0.059(2)
C15	1.0070(3)	0.3455(6)	0.3749(4)	0.067(2)
C16	1.0022(3)	0.1039(7)	0.3823(5)	0.080(3)
C17	0.6980(2)	0.2366(6)	0.1860(3)	0.051(2)
C18	0.6205(3)	0.233(2)	0.1760(5)	0.147(6)
C19	0.7046(7)	0.121(2)	0.129(1)	0.28(1)
C20	0.7027(6)	0.359(2)	0.1389(9)	0.221(7)
C21	0.6553(2)	0.1669(4)	0.6321(3)	0.042(2)
C22	0.6936(3)	0.1213(5)	0.7226(4)	0.056(2)
C23	0.7048(3)	0.2022(6)	0.7998(4)	0.067(2)
C24	0.6795(3)	0.3230(6)	0.7900(4)	0.069(3)
C25	0.6411(3)	0.3701(5)	0.7022(4)	0.063(2)
C26	0.6286(3)	0.2936(5)	0.6229(4)	0.051(2)
C27	0.6154(2)	−0.0484(4)	0.5556(3)	0.039(2)
C28	0.5650(3)	−0.0683(5)	0.5997(4)	0.053(2)
C29	0.5383(3)	−0.1898(6)	0.6043(4)	0.065(2)
C30	0.5623(3)	−0.2944(5)	0.5673(4)	0.069(2)
C31	0.6131(3)	−0.2763(5)	0.5237(4)	0.068(2)
C32	0.6397(3)	−0.1541(5)	0.5184(4)	0.054(2)

---

[a] Numbers in parentheses are estimated standard deviations.

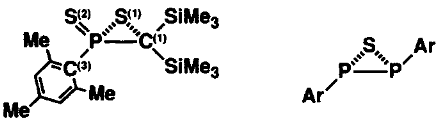
[b] Equivalent isotropic U is defined as one-third the trace of the orthogonalized U_{ij} tensor.

measured on a Hitachi 340 spectrometer. The mass spectra were obtained on a JEOL JMS-D-300 spectrometer employing electron impact ionization (70 eV). The melting point reported here is uncorrected.

Preparation of 3-Diphenylmethylene-2-(2,4,6-tri-t-butylphenyl)thiaphosphirane 2-Sulfide (**3**)

The starting material, 3,3-diphenyl-1-(2,4,6-tri-*t*-butylphenyl)-1-phosphaallene (**1**) was prepared either by the reaction of lithium (*t*-butyldimethylsilyl)(2,4,6-tri-*t*-butylphenyl)phosphide with diphenyl-ketene [3] or by the reaction of 1 - trimethylsilyl - 2 - (2,4,6 - tri - *t* - butylphenyl) - 2 - phosphaethenyl-lithium with benzophenone [6]. To a solution of **1** (62.1 mg, 0.14 mmol) and elemental sulfur (15.1 mg, 0.47 mg-atom) in benzene (8 ml) was added one drop of 1,8-diazabicyclo [5.4.0]undec-7-ene (DBU) via a syringe. The reaction mixture turned red, and the ^{31}P NMR spectrum of the mixture of an early stage gave an intermediate signal at δ_P 79 due to the presence of the 1-phosphaallene 1-sulfide **2**. After the mixture had been stirred for 12 h, the solvent was evaporated in vacuo. Chromatographic separation gave 54.3 mg of the methylenethiaphosphirane 2-sulfide **3** (77%). **3**: mp 143–145°C; ^{1}H NMR (CDCl$_3$) δ 7.7–7.6 (2H, m, arom.), 7.5–7.3 (4H, m, arom.), 7.3–7.1 (6H, m, arom.), 1.78 (9H, s, o-Bu^t), 1.30 (9H, s, p-Bu^t), and

SCHEME 3



5 **6**

1.21 (9H, s, o'-Bu^t); ^{31}P NMR (CDCl$_3$) δ_P -18.9 (s); ^{13}C {^{1}H} NMR (CDCl$_3$) δ 155.2 (d, $^2J_{PC}$ = 9.8 Hz, o-Ar), 152.5 (d, $^4J_{PC}$ = 4.5 Hz, p-Ar), 152.3 (d, $^2J_{PC}$ = 10.5 Hz, o'-Ar), 141.3 (d, $^3J_{PC}$ = 2.1 Hz, ipso-Ph), 141.1 (d, $^2J_{PC}$ = 16.2 Hz, PC=*C*), 140.1 (d, $^3J_{PC}$ = 4.2 Hz, ipso'-Ph), 134.0 (d, $^1J_{PC}$ = 84.2 Hz, ipso-Ar), 131.6 (s, Ph), 129.2 (s, Ph), 128.6 (s, Ph), 128.3 (s, Ph), 128.2 (s, Ph), 128.0 (s, Ph), 125.4 (d, $^1J_{PC}$ = 64.3 Hz, P*C*=C), 124.8 (d, $^3J_{PC}$ = 16.1 Hz, m-Ar), 123.3 (d, $^3J_{PC}$ = 16.4 Hz, m'-Ar), 40.7 (d, $^3J_{PC}$ = 2.3 Hz, o-*C*Me$_3$), 38.6 (d, $^3J_{PC}$ = 3.2 Hz, o'-*C*Me$_3$), 34.9 (d, $^5J_{PC}$ = 1.6 Hz, p-*C*Me$_3$), 34.6 (s, o-C*Me*$_3$), 33.6 (s, o'-C*Me*$_3$), 31.0 (s, p-C*Me*$_3$); IR (KBr) 771, 735, 700, 690, 658 cm^{-1}; MS *m*/*z* 518 (M$^+$); UV (hexane) λ_{max} 243 (ε 28400) and 322 nm (9800). Found: m/z 518.2242. Calcd for $C_{32}H_{39}PS_2$: M, 518.2231.

*X-Ray Structure Determination of **3***

Compound **3** was recrystallized from toluene at 0°C. $C_{32}H_{39}PS_2$, M = 518.77, monoclinic, space group $P2_1/n$, a = 19.809(6), b = 10.389(4), c = 14.937(4) Å, β = 109.34(2)°, U = 2900(2) Å^3, Z = 4, Dc = 1.188 g cm^{-3}. 5153 Reflections with $2\theta \leq 50°$ were recorded on a four-circle diffractometer using graphite-monochromated Mo-Kα radiation using the $\omega/2\theta$ scan mode. Of these, 3467 [with $I > 3\sigma(I)$] were judged as observed. Three reference reflections monitored every 180 min displayed neither systematic nor significant deviations from their initial intensities. The intensities were corrected for Lorentz and polarization factors, but no absorption correction was applied. The structure was solved using MULTAN 80 [15]. Full-matrix least-squares refinement with anisotropic temperature factors for nonhydrogen atoms converged to R = 0.064 and R_w = 0.072 [16]. The hydrogen atoms of the *t*-butyl group bonded to C(8) could not be located because of large thermal motion of this group.

ACKNOWLEDGMENTS

This work was supported in part by the Grant-in-Aids for Scientific Research (No. 01470021 and 01648001) from the Ministry of Education, Science and Culture, Japan. The authors thank the Research Centre for Protein Engineering, Institute for Protein Research at Osaka University for computer calculations. They thank Shin-Etsu Chemical Co., Ltd., for donating organosilicon compounds and Tosoh Akzo Chemical Co. Ltd., for organolithium reagents.

SUPPLEMENTARY MATERIAL AVAILABLE

Tables of anisotropic thermal parameters, H-atom coordinates, bond distances and angles, and structure factors for **3** (10 pages) have been deposited with CCDC. Ordering information is given on any current masthead page.

REFERENCES

[1] G. L'abbé, *Angew. Chem., Int. Ed. Engl., 19,* 1980, 276.

[2] M. Yoshifuji, K., Toyota, N. Inamoto, *Tetrahedron Lett., 26,* 1985, 1727.

[3] M. Yoshifuji, K. Toyota, K. Shibayama, N. Inamoto, *Tetrahedron Lett., 25,* 1984, 1809.

[4] M. Yoshifuji, K. Toyota, N. Inamoto, *J. Chem. Soc., Chem. Commun.,* 1984, 689.

[5] M. Yoshifuji, S. Sasaki, T. Niitsu, N. Inamoto, *Tetrahedron Lett., 30,* 1989, 187.

[6] M. Yoshifuji, S. Sasaki, N. Inamoto, *Tetrahedron Lett., 30,* 1989, 839.

[7] M. Yoshifuji, K. Toyota, N. Inamoto, K. Hirotsu, T. Higuchi, S. Nagase, *Phosphorus Sulfur, 25,* 1985, 237.

[8] E. Niecke, D.-A. Wildbredt, *J. Chem. Soc., Chem. Commun.,* 1981, 72.

[9] M. Caira, R. H. Neilson, W. H. Watson, P. W.-Neilson, Z.-M. Xie, *J. Chem. Soc., Chem. Commun.,* 1984, 698.

[10] (a) M. Yoshifuji, K. Shibayama, N. Inamoto, K. Hirotsu, T. Higuchi, *J. Chem. Soc., Chem. Commun.,* 1983, 862; (b) M. Yoshifuji, K. Shibayama, N. Inamoto, *Heterocycles, 22,* 1984, 681.

[11] (a) E. Jongejan, Th. S. V. Buys, H. Steinberg, Th. J. de Boer, *Recl. Trav. Chim. Pays-Bas, 97,* 1978, 214; (b) E. Block, R. E. Penn, M. D. Ennis, T. A. Owens, S.-L. Yu, *J. Am. Chem. Soc., 100,* 1978, 7436; (c) W. Ando, Y. Hanyu, T. Furuhata, T. Takata, *J. Am. Chem. Soc., 105,* 1983, 6151.

[12] C. K. Johnson, *ORTEP, Oak Ridge National Laboratory Report,* ORNL-TM-3794, 1965.

[13] M. Yoshifuji, K. Ando, K. Shibayama, N. Inamoto, K. Hirotsu, T. Higuchi, *Angew. Chem., Int. Ed. Engl., 22,* 1983, 418.

[14] R. Appel, P. Fölling, B. Josten, M. Siray, V. Winkhaus, F. Knoch, *Angew. Chem., Int. Ed. Engl., 23,* 1984, 619.

[15] P. Main, S. J. Fiske, S. E. Hull, L. Lessinger, G. Germain, J.-P. Declercq, M. M. Woolfson, *MULTAN 80. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data,* Universities of York, England, and Louvain, Belgium, 1980.

[16] W. R. Busing, K. O. Martin, H. S. Levy, *ORFLS, Oak Ridge National Laboratory Report,* ORNL-TM-305, 1965.