CHEMISTRY LETTERS, pp. 2213-2216, 1991.

Isolation and X-Ray Structure of *trans*-3,5-Bis(2,4,6-tri-*t*-butylphenyl)-1,2,3,5-dithiadiphospholane 3,5-Disulfide

Kozo TOYOTA, Yasuhisa ISHIKAWA, Masaaki YOSHIFUJI,* Kengo OKADA,† Keiji HOSOMI,† and Ken HIROTSU*†

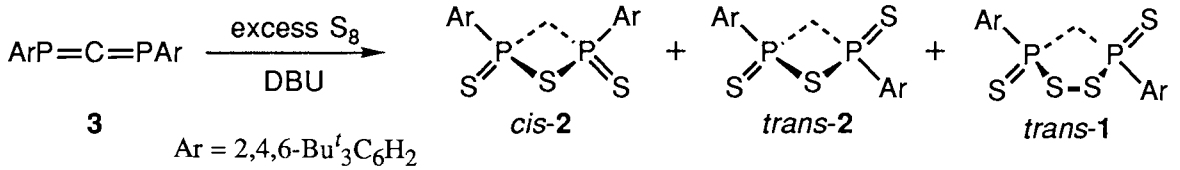
Department of Chemistry, Faculty of Science, Tohoku University, Aoba, Sendai 980

† Department of Chemistry, Faculty of Science, Osaka City University, Sumiyoshi, Osaka 558

A phosphorus-containing novel heterocyclic compound, *trans*-3,5-bis(2,4,6-tri-*t*-butylphenyl)-1,2,3,5-dithiadiphospholane 3,5-disulfide (*trans*-**1**), was isolated in the reaction of 1,3-bis(2,4,6-tri-*t*-butylphenyl)-1,3-diphosphaallene with sulfur and the structure of *trans*-**1** was confirmed by the X-ray crystallography. Desulfurization of *trans*-**1** afforded the corresponding *trans*-1,2,4-thiadiphosphetane 2,4-disulfide.

Phosphorus-containing small ring compounds such as oxaphosphetanes are of current interest in connection with the study of intermediates in the Wittig type of reactions.[1] Such compounds are generally highly reactive and steric protection with bulky substituents is one of the promising methods for the kinetic stabilization.[2] Recently, we have reported the isolation and characterization of *cis*-2,4-bis(2,4,6-tri-*t*-butylphenyl)-1,2,4-thiadiphosphetane 2,4-disulfide (*cis*-**2**)[3] which was obtained in the reaction of 1,3-bis(2,4,6-tri-*t*-butylphenyl)-1,3-diphosphaallene (**3**)[4] with elemental sulfur in the presence of a base[5] such as 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU). The structure of *cis*-**2** was unambiguously confirmed by means of the X-ray crystallography. We now report here the isolation and the X-ray analysis of the *trans*-3,5-bis(2,4,6-tri-*t*-butylphenyl)-1,2,3,5-dithiadiphospholane 3,5-disulfide (*trans*-**1**) as a novel heterocyclic compound containing phosphorus and the isolation and characterization of the *trans*-2,4-bis(2,4,6-tri-*t*-butylphenyl)-1,2,4-thiadiphosphetane 2,4-disulfide (*trans*-**2**).

In the reaction of the diphosphaallene **3** with sulfur in toluene at room temperature in the presence of DBU the *trans*-**1** was obtained in only low yield (2.2% yield based on **3**). At the same time in this reaction, *trans*-**2** was also formed as a minor product (0.5%), besides *cis*-**2** (35.0%) as a major product. *trans*-**1**: Mp 208 – 210 °C (decomp.); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.25 (4H, bs, arom.), 3.96 (2H, t, $^2J_{PH}$ = 9.6 Hz, PCH_2P), 1.55 (18H, bs, *o*-Bu^t), 1.48 (18H, bs, *o*'-Bu^t), and 1.29 (18H, s, *p*-Bu^t); ^{31}P{^{1}H} NMR (81 MHz, $CDCl_3$) δ 87.6; ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 160.2 (bs, *o*-arom.), 159.5 (bs, *o*'-arom.), 153.0 (pseudo t, J_{PC} = 2.1 Hz, *p*-arom.), 127.3 (dd, $^1J_{PC}$ = 90.0 Hz, $^3J_{PC}$ = 13.0 Hz, *ipso*-arom.), 124.8 (bs, *m*-arom.),



123.8 (bs, *m*'-arom.), 62.6 (t, $^1J_{PC}$ = 53.4 Hz, PCP), 42.4 (bs, *o*-$\underline{C}Me_3$), 41.7 (bs, *o*'-$\underline{C}Me_3$), 34.7 (s, *p*-$\underline{C}Me_3$), 34.6 (bs, *o*-C$\underline{Me}_3$), 34.2 (bs, *o*'-C$\underline{Me}_3$), and 30.9 (s, *p*-C$\underline{Me}_3$); IR (KBr) 758 and 646 cm^{-1}; MS *m/z* (rel intensity) 694 (M^+; 5), 637 (M^+–Bu^t; 38), and 581 (MH^+–2Bu^t; 100); Found: *m/z* 694.3055. Calcd for $C_{37}H_{60}P_2S_4$: M, 694.3053. *trans*-**2**: Mp 236 – 237.5 °C (decomp.); ^{1}H NMR ($CDCl_3$) δ 7.31 (2H, d, $^4J_{PH}$ = 2.2 Hz, arom.), 7.29 (2H, d, $^4J_{PH}$ = 2.9 Hz, arom.), 4.48 (2H, t, $^2J_{PH}$ = 12.2 Hz, PCH_2P), 1.52 (18H, s, *o*-Bu^t), 1.51 (18H, s, *o*'-Bu^t), and 1.33 (18H, s, *p*-Bu^t); ^{31}P{^{1}H} NMR ($CDCl_3$) δ 45.1; ^{13}C{^{1}H} NMR ($CDCl_3$) δ 157.4 (s, *o*-arom.), 154.0 (pseudo t, J_{PC} = 4.3 Hz, *o*'-arom.), 152.7 (s, *p*-arom.), 134.4 (d, $^1J_{PC}$ = 78.8 Hz, *ipso*-arom.), 125.2 (t, J_{PC} = 7.0 Hz, *m*-arom.), 124.3 (t, J_{PC} = 7.3 Hz, *m*'-arom.), 73.4 (t, $^1J_{PC}$ = 46.5 Hz, PCP), 41.6 (s, *o*-$\underline{C}Me_3$), 40.5 (s, *o*'-$\underline{C}Me_3$), 34.9 (s, *o*-C$\underline{Me}_3$), 34.7 (s, *p*-$\underline{C}Me_3$), 34.6 (s, *o*'-C$\underline{Me}_3$), and 31.1 (s, *p*-C$\underline{Me}_3$); IR (KBr) 785, 758, 642, and 631 cm^{-1}; MS *m/z* (rel intensity) 662 (M^+; 3) and 605 (M^+–Bu^t; 100); Found: *m/z* 662.3339. Calcd for $C_{37}H_{60}P_2S_3$: M, 662.3332. The methylene protons of both *trans*-**1** and *trans*-**2** are magnetically equivalent indicating that the both take *trans* configurations. Furthermore, hindered rotation of the 2,4,6-tri-*t*-butylphenyl group (hereafter abbreviated to Ar group) in ^{1}H and ^{13}C NMR spectra were observed in either compound at room temperature as has been observed in **3**.[6]

The structure of *trans*-**1** was unambiguously established by X-ray crystallographic analysis.[7] Figure 1 shows the ORTEP drawing of the molecular structure for *trans*-**1**.[8] Selected bond lengths and angles, dihedral angles, and intramolecular short contacts are listed in the caption of Fig. 1. The molecule has an approximate two-fold axis, which goes through C1 and the middle point of S1–S2 bond, except for *p*-*t*-butyl groups. The central five-membered ring (C1, P1, P2, S1, and S2) takes a half-chair form, where S1 and S2 deviate by 0.524(9) and 0.719(9) Å toward the opposite direction, respectively, from the plane defined by C1, P1, and P2. Two bulky Ar are in *trans* positions to the central ring, and cover the central ring from both sides. The atoms, C2, P1, P2, and C20, are coplanar within 0.10(1) Å and phenyl rings, (C2–C7) and (C20–C25), make angles of 75.0 and 75.1° with this plane, respectively.

The bulky *o*-*t*-butyl groups in the Ar moieties have unusually short intramolecular contacts with the central part of the molecule (see the caption of Fig. 1). These short contacts cause the large deformation of Ar groups to the boat forms, which is commonly observed for the Ar-P containing compounds.[9] The atoms, C3, C4, C6, and C7 are coplanar within 0.004(6) Å, with P1, C2, and C5 deviating by 1.29(1), 0.21(1), and 0.10(1) Å, respectively. This plane makes angles of 17.0 and 8.1° with the plane [C3, C2, and C7] and the plane [C4, C5, and C6], respectively. Similarly, the atoms, C21, C22, C24, and C25, are coplanar within 0.001 Å, with P2, C20, and C23 deviating by 1.37(1), 0.23(1), and 0.11(1) Å, respectively. The bow and the stern of this boat-shaped benzene ring bend up by 18.8 and 8.7° from the bottom. These deformation angles of the phenyl rings to the boat forms are comparable to the average values of 18.5 and 10.3° for bis(2,4,6-tri-*t*-butylphenyl)phosphinic chloride,[10] where large deformation is found for non-bridged benzene derivatives.

The endocyclic P–C bonds [1.844(6) and 1.830(6) Å] are significantly shorter than 1.872(8) and 1.867(7) Å for *cis*-**2**[3] and the P–C distances, 1.872(3), 1.873(3), 1.881(3), and 1.914(3) Å in 2,4-bis(dimethylamino)-1,3-diphenyl-1,3-diphosphetane.[11] The P–S bond lengths [2.116(3) and 2.112(3) Å] within the central ring are comparable to 2.101(2) Å for 3-diphenylmethylene-2-(2,4,6-tri-*t*-butylphenyl)-1,2-thiaphosphirane 2-sulfide (**5**),[12] 2.103(3) Å for *trans*-2,3-bis(2,4,6-tri-*t*-butylphenyl)-1,2,3-thiadiphosphirane,[13] and 2.120(3) and 2.127(3) Å for *cis*-**2**,[3] but considerably longer than 2.049(3) Å for 2-mesityl-3,3-bis(trimethylsilyl)-1,2-thiaphosphirane 2-sulfide.[14] The exocyclic P=S bonds [1.939(2) and 1.936(3) Å] are slightly longer than 1.923(3) and 1.926(3) Å for *cis*-**2**[3] and 1.923(2) Å for **5**.[12]

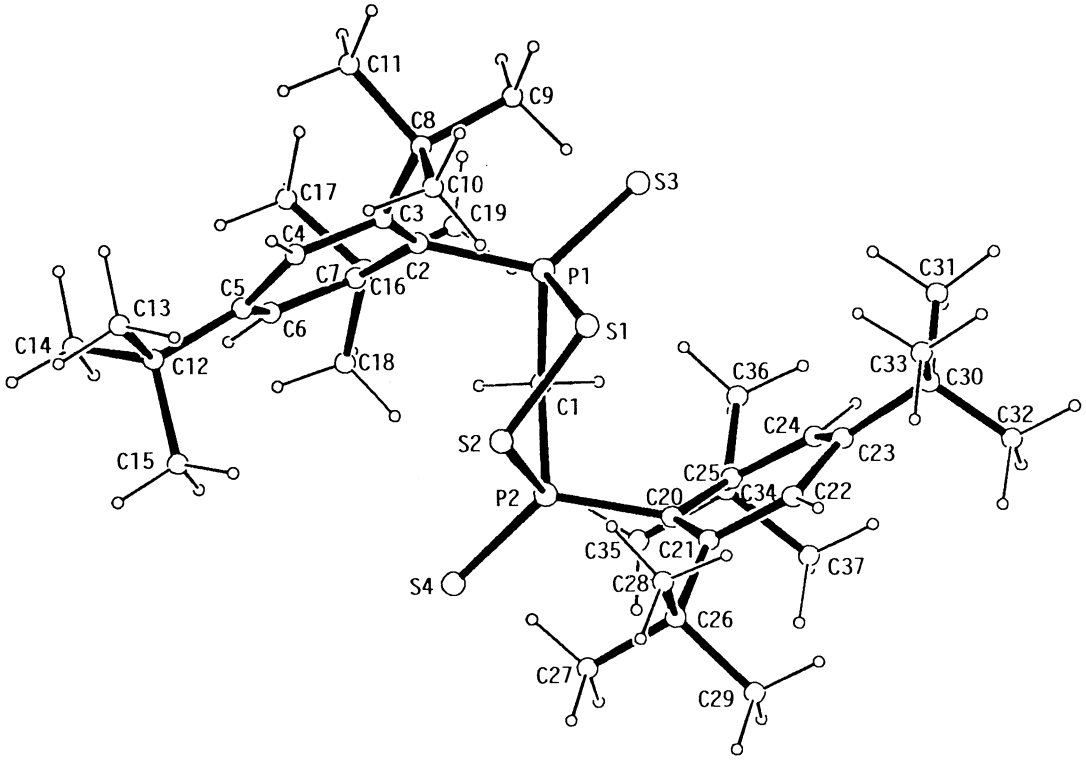


Fig. 1. Molecular structure of the 1,2,3,5-dithiadiphospholane 3,5-disulfide (*trans*-**1**). Bond length / Å: P1–S1, 2.116(3); P1–S3, 1.939(2); P1–C1, 1.844(6); P1–C2, 1.852(4); P2–S2, 2.112(3); P2–S4, 1.936(3); P2–C1, 1.830(6); P2–C20, 1.850(4); S1–S2, 2.044(2). Bond angle / °: P1–C1–P2, 119.6(4); S1–P1–C1, 97.3(2); S2–P2–C1, 97.1(2); P1–S1–S2, 96.7(1); P2–S2–S1, 96.2(1); S1–P1–S3, 107.8(1); S1–P1–C2, 106.1(2); S3–P1–C1, 113.6(2); S3–P1–C2, 125.5(2); C1–P1–C2, 102.9(2); S2–P2–S4, 107.8(1); S2–P2–C20, 105.3(2); S4–P2–C1, 112.5(2); S4–P2–C20, 126.6(2); C1–P2–C20, 103.5(2). Dihedral angle /°: S1–P1–C1–P2, 14.5(3); P1–C1–P2–S2, 20.1(3); C1–P2–S2–S1, –46.2(2); P2–S2–S1–P1, 54.8(1); S2–S1–P1–C1, –43.3(2); C2–P1···P2–C20, –167.9(3); P1–C2–C3–C8, 48.5(7); P1–C2–C7–C16, –49.8(7); P2–C20–C21–C26, 51.2(8); P2–C20–C25–C34, –53.6(7). Short contact / Å: P1···C9, 3.223(8); P1···C19, 3.222(8); P2···C27, 3.241(8); P2···C35, 3.223(8); S1···C9, 3.421(7); S2···C27, 3.465(7); S3···C9, 3.435(7); S4···C27, 3.465(9); C1···C16, 3.336(8); C1···C19, 3.226(9); C1···C34, 3.360(7); C1···C35, 3.27(1).

The *trans*-thiadiphosphetane disulfide *trans*-**2** was also formed by base induced desulfurization reaction of *trans*-**1** with DBU in toluene at room temperature for 24 h in 55% yield after silica-gel column chromatography, indicating that the configuration around the phosphorus atoms was retained during this desulfurization procedure.[15] On the other hand, attempted sulfurization of *trans*-**2** with excess amount of sulfur in the presence of DBU at room temperature for 20 h or in the absence of DBU in refluxing benzene for 2 h resulted in the almost quantitative recovery of *trans*-**2**.

This work was supported in part by the Grants-in-Aid for Scientific Research No. 01648001 and No. 02403008 from the Ministry of Education, Science and Culture, Japanese Government. The authors thank the Research Centre for Protein Engineering, Institute for Protein Research at Osaka University for computer calculation. They also thank Tosoh Akzo Co., Ltd. for donating organolithium reagents throughout this work.

References

1) See, for example: B. E. Maryanoff and A. B. Reitz, *Chem. Rev.*, **89**, 863 (1989).

2) "Multiple Bonds and Low Coordination in Phosphorus Chemistry," ed by M. Regitz and O. J. Scherer, Georg Thieme Verlag, Stuttgart (1990).

3) K. Toyota, M. Yoshifuji, and K. Hirotsu, *Chem. Lett.*, **1990**, 643.

4) M. Yoshifuji, K. Toyota, and N. Inamoto, *J. Chem. Soc., Chem. Commun.*, **1984**, 689; H. H. Karsch, F. H. Köhler, and H.-U. Reisacher, *Tetrahedron Lett.*, **25**, 3687 (1984); R. Appel, P. Fölling, B. Josten, M. Siray, V. Winkhaus, and F. *Knoch, Angew. Chem., Int. Ed. Engl.*, **23**, 619 (1984).

5) See, for example: R. Sato, T. Goto, Y. Takikawa, and S. Takizawa, *Synthesis*, **1980**, 615; M. Yoshifuji, K. Shibayama, N. Inamoto, K. Hirotsu, and T. Higuchi, *J. Chem. Soc., Chem. Commun.*, **1983**, 862; N. Tokitoh, M. Noguchi, Y. Kabe, W. Ando, M. Goto, and H. Maki, *Tetrahedron Lett.*, **31**, 7641 (1990).

6) M. Yoshifuji, S. Sasaki, T. Niitsu, and N. Inamoto, *Tetrahedron Lett.*, **30**, 187 (1989).

7) *Crystal data*: $C_{37}H_{60}P_2S_4$, M = 695.09, monoclinic, space group $P2_1/c$, a = 20.047(4), b = 12.041(2), c = 19.173(3) Å, β = 117.35(1)°, U = 4111(1) Å^3, Z = 4, Dc = 1.123 g cm^{-3}, μ = 29.98 cm^{-1}. 6094 Reflections with $2\theta \leq 120°$ were recorded on a four circle diffractometer using graphite-monochromated Cu-$K\alpha$ radiation. Of these, 4476 [with $I > 3\sigma(I)$] were judged as observed. The structure was solved using SHELX.[16] All hydrogen atoms could be located on a difference Fourier synthesis. Full-matrix least-squares refinement with anisotropic temperature factors for non-hydrogen atoms and isotropic hydrogens converged to R = 0.061 and Rw = 0.067.[17] Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW, U. K.

8) C. K. Johnson, ORTEPII, *Oak Ridge National Laboratory Report*, ORNL-TM-5138, 1976.

9) M. Yoshifuji, N. Inamoto, K. Hirotsu, and T. Higuchi, *J. Chem. Soc., Chem. Commun.*, **1985**, 1109.

10) M. Yoshifuji, I. Shima, N. Inamoto, K. Hirotsu, and T. Higuchi, *Angew. Chem., Int. Ed. Engl.*, **19**, 399 (1980).

11) G. Becker, W. Massa, O. Mundt, and R. Schmidt, *Z. Anorg. Allg. Chem.*, **485**, 23 (1982).

12) K. Hirotsu, A. Okamoto, K. Toyota, and M. Yoshifuji, *Heteroatom Chem.*, **1**, 251 (1990).

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

14) M. Caira, R. H. Neilson, W. H. Watson, P. W.-Neilson, and Z.-M. Xie, *J. Chem. Soc., Chem. Commun.*, **1984**, 698.

15) This observed total retention of configuration does not necessarily indicate that the desulfurization reaction should not involve any inversion process. The mechanistic study of this reaction is in progress.

16) G. M. Sheldrick, SHELX86: Program for the Automatic Solution of Crystal Structures. University of Göttingen, Federal Republic of Germany, 1986.

17) W. R. Busing, K. O. Martin, and H. S. Levy, ORFLS, *Oak Ridge National Laboratory Report*, ORNL-TM-305, 1965.

(Received September 21, 1991)