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Preparation and X-Ray Crystal Structure Analysis of *cis*-2,4-Bis(2,4,6-tri-*t*-butylphenyl)-1,2,4-oxadiphosphetane 2,4-Disulfide and *cis/trans* Isomerization of the Corresponding 1,2,4-Thiadiphosphetane Derivative

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ABSTRACT

*1,3-Bis(2,4,6-tri-t-butylphenyl)-1,3-diphosphaallene (**1**) reacted with elemental sulfur under wet reaction conditions to give cis- and trans-2,4-bis(2,4,6-tri-t-butylphenyl)-1,2,4-thiadiphosphetane 2,4-disulfide (cis-**2** and trans-**2**) and cis-2,4-bis(2,4,6-tri-t-butylphenyl)-1,2,4-oxadiphosphetane 2,4-disulfide (cis-**3**). The structure of cis-**3** was determined by X-ray crystallography, and the cis/trans isomerization of **2** was studied.*

INTRODUCTION

Phosphorus compounds in low coordination states are of current interest, and multiple bonded P(III)-compounds, such as phosphaalkenes, phosphaalkynes, and diphosphenes, have been extensively investigated in terms of unusual structure and reactivity [1]. Kinetic stabilization with bulky substituents has turned out to be effective in stabilizing such compounds, and this strategy has been widely used to prepare phosphacumulenes, such as phosphaallenes $ArP{=}C{=}CR_1R_2$ [2–4], azaphosphaallenes $ArP{=}C{=}NR$ [2,5], phosphaketene $ArP{=}C{=}O$ [6], and diphosphaallenes $ArP{=}C{=}PR$ [7], with an extremely bulky 2,4,6-tri-*t*-butylphenyl (abbreviated to the Ar group) as a protecting group. We have recently reported that 1,3-bis(2,4,6-tri-*t*-butylphenyl)-1,3-diphosphaallene (**1**) reacted with elemental sulfur in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) to give *cis*-2,4-bis(2,4,6-tri-*t*-butylphenyl)-1, 2, 4-thiadiphosphetane 2,4-disulfide (*cis*-**2**) [8]. We report here that this sulfurization reaction of **1** had also produced another new type of heterocyclic compound, *cis*-2,4-bis(2,4,6-tri-*t*-butylphenyl)-1, 2, 4-oxadiphosphetane 2,4-disulfide (*cis*-**3**). The crystal structure analysis of *cis*-**3** has been carried out for the first time. Moreover, we have observed *cis/trans* isomerization between *cis*-**2** and *trans*-**2**.

Dedicated to Prof. James Cullen Martin on the occasion of his sixty-fifth birthday.

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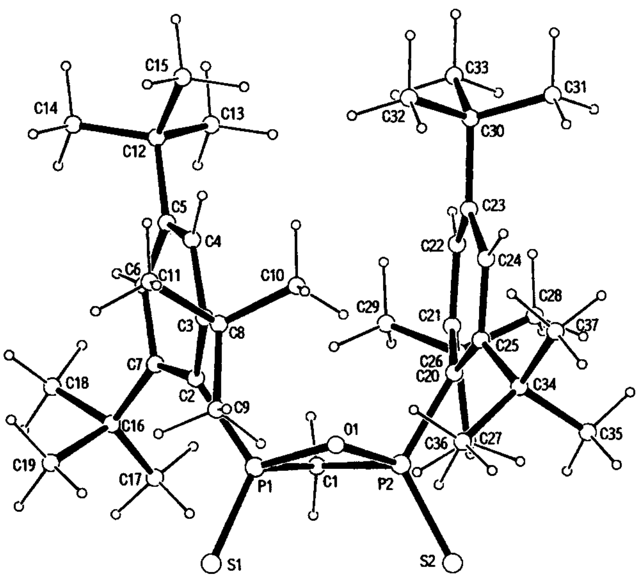
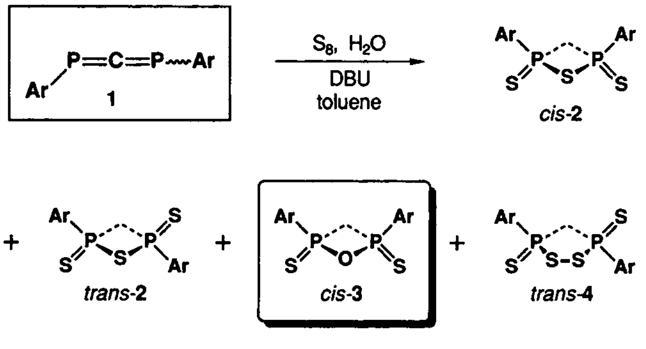


FIGURE 1 X-Ray structure of *cis*-**3** showing the atom labeling scheme.

RESULTS AND DISCUSSION

The reaction of 1,3-diphosphaallene **1** with elemental sulfur in the presence of DBU in toluene at ambient temperature gave *cis*-**2** (36% yield) as a major product [8], together with its *trans*-isomer (*trans*-**2**; 3%), the oxadiphosphetane *cis*-**3** (13%), and *trans*-1,2,3,5-dithiadiphospholane 3,5-disulfide (*trans*-**4**; 12%) [9]. The sulfurization of **1** did not proceed at room temperature either in the absence of a base or in the presence of a weak base, such as lutidine or triethylamine. At a higher temperature in triethylamine, **1** reacted with sulfur to give *cis*-**2** (17%), *trans*-**2** (1%), *cis*-**3** (3%), and *trans*-**4** (4%).

The compound *cis*-**3** possesses a hitherto unknown oxadiphosphetane skeleton, and its ring structure was confirmed by X-ray crystallography. Figure 1 is an ORTEP drawing [10] of *cis*-**3**. Some selected bond lengths and angles, dihedral angles, and intramolecular short contacts are listed in Table 1. Table 2 shows fractional coordinates and temperature factors for *cis*-**3**. The overall structure of *cis*-**3** is similar to that of *cis*-**2** [8], although the smaller size of the central oxadiphosphetane ring of *cis*-**3** than the thiadiphosphetane ring of *cis*-**2** makes the two bulky Ar groups on the phosphorus atoms approach each other more closely. The four-membered ring (P1, O1, P2, and C1) has a puckered form rather than a planar one, as is seen from the dihedral angles listed in Table 1. The puckering angle between the plane (P1, O1, and C1) and the plane (P2, O1, and C1) is 18.4° (as compared to 19.2° in *cis*-**2**). Four bulky *o*-*t*-butyl groups cover the central four-membered ring from both sides (C1 and O1 sides). The two Ar rings are approximately perpendicular (av 86.3°) to the basic oxaphosphetane ring. These two phenyl rings rotate by 11.7° from the parallel orientation, resulting in the opening of the C6–C7 and C21–C22 side and closing of the C3–C4 and C24–C25 side. This is due to the extremely short contacts between C1 and C17 (3.17(2) Å) and between C1 and C27 (3.17(1) Å). The unusual short contacts among four *o*-*t*-butyl groups and the oxaphosphetane ring (see Table 1) cause the deformation of the two bulky phenyl rings into the boat forms, which is commonly observed in the Ar-P containing compounds [11]. The atoms C3, C4, C6, and C7 are coplanar within 0.00(1) Å with P1, C2, and C5 deviating by 1.03(2), 0.18(1), and 0.09(1) Å, respectively. Similarly, the atoms C21, C22, C24, and C25 are coplanar within 0.01(1) Å with P2, C20, and C23 deviating by 1.01(1), 0.17(1), and 0.09(1) Å, respectively. The former plane makes an angle of 15.0° with the plane (C2, C3, and C7) and the latter plane 14.1° with the plane (C20, C21, and C25). These deformation angles are almost equal to an average value of 15.3° for *cis*-**2** and comparable to an average value of 18.5° for bis(2,4,6-tri-*t*-butylphenyl)phosphinic chloride [12], where a large deformation is found for nonbridged benzene derivatives. The average distance (1.915(3) Å) of the P=S bonds is slightly shorter than the av 1.925(2) for *cis*-**2** [8] and 1.932(3) Å for 2-mesityl-3,3-bis(trimethylsilyl)thiaphosphirane 2-sulfide [13]. The endocyclic P–C bonds (av 1.84(1) Å) are shorter than 1.872(8) and 1.867(7) Å for *cis*-**2** and the average distance of 1.889 Å for 1,3-diphosphetane derivatives [14]. There are no intermolecular nonhydrogen-atom contacts less than 3.62(1) Å.



Ar = 2,4,6-Bu$^t_3$C$_6$H$_2$; DBU = 1,8-diazabicyclo[5.4.0]undec-7-ene

SCHEME 1

The oxygen atom of *cis*-**3** seems to have been derived from moisture present during the reaction. The similar sulfurization reaction of **1** in toluene in the presence of DBU and H$_2$^{18}O (^{18}O content: 80.3 at. %) gave a mixture of *cis*-**3** and *cis*-**3**-^{18}*O* in 32% yield. The ^{18}O content of the product (*cis*-**3** and *cis*-**3**-^{18}*O*) was determined to be 63%, as determined by means of the MS spectrum. It should be noted here that the attempted conversion of *cis*-**3** to *cis*-

TABLE 1 Selected Bond Distances and Angles, Dihedral Angles, and Intramolecular Short Contacts for **5**[a]

Bond Distance/Å		*Bond Angle/°*		*Dihedral Angle/°*		*Intramolecular Short Contact/Å*	
P1-C1	1.85(1)	O1-P1-C1	83.9(4)	C1-P1-O1-P2	−14.5(3)	P1···C9	3.13(1)
P2-C1	1.83(1)	O1-P2-C1	84.5(4)	P1-O1-P2-C1	14.7(3)	P2···C27	3.16(1)
P1-O1	1.634(6)	P1-O1-P2	101.3(4)	O1-P2-C1-P1	−12.7(3)	P2···C36	3.32(1)
P2-O1	1.643(7)	P1-C1-P2	87.1(5)	P2-C1-P1-O1	12.8(3)	O1···C9	3.02(1)
P1-S1	1.908(3)	S1-P1-C2	121.9(2)	P2-P1-C2-C3	−68.2(7)	C1···C17	3.17(2)
P2-S2	1.922(4)	S2-P2-C20	122.1(3)	P2-P1-C2-C7	97.6(6)	S1···C27	3.17(1)
P1-C2	1.837(8)			P1-P2-C20-C21	−79.3(7)		
P2-C20	1.820(6)			P1-P2-C20-C25	85.4(7)		

[a] Numbers in parentheses are estimated standard deviations.

TABLE 2 Fractional Coordinates and Equivalent Isotropic Displacement Coefficients (Å^2) for **5**

Atom	X^a	Y^a	Z^a	$U(eq)^{a,b}$	*Atom*	X^a	Y^a	Z^a	$U(eq)^{a,b}$
P1	0.1832(2)	0.2936(2)	0.4589(2)	0.065(1)	C17	0.346(1)	0.484(1)	0.463(2)	0.21(1)
P2	−0.0528(2)	0.3215(2)	0.4093(2)	0.060(1)	C18	0.482(1)	0.474(1)	0.353(1)	0.152(9)
S1	0.2838(3)	0.2741(4)	0.6230(2)	0.132(2)	C19	0.509(1)	0.374(1)	0.490(1)	0.135(7)
S2	−0.1063(3)	0.3301(3)	0.5445(2)	0.106(2)	C20	−0.1666(6)	0.3096(5)	0.2572(6)	0.047(3)
O1	0.0463(5)	0.2438(4)	0.4129(4)	0.063(2)	C21	−0.1778(7)	0.3749(6)	0.1734(8)	0.056(3)
C1	0.0824(7)	0.3901(7)	0.4204(7)	0.067(4)	C22	−0.2102(9)	0.3510(6)	0.0528(7)	0.064(4)
C2	0.2513(6)	0.2862(5)	0.3407(5)	0.043(3)	C23	−0.2392(8)	0.2700(6)	0.0132(7)	0.065(4)
C3	0.2192(7)	0.2174(5)	0.2606(6)	0.045(3)	C24	−0.2513(8)	0.2112(6)	0.0955(8)	0.059(4)
C4	0.2153(7)	0.2328(5)	0.1427(6)	0.050(3)	C25	−0.2189(7)	0.2291(6)	0.2165(7)	0.056(3)
C5	0.2496(7)	0.3082(5)	0.1084(6)	0.048(3)	C26	−0.1797(9)	0.4740(6)	0.1911(9)	0.072(4)
C6	0.3048(8)	0.3684(5)	0.1964(7)	0.054(3)	C27	−0.169(1)	0.5025(7)	0.319(1)	0.093(6)
C7	0.3113(7)	0.3592(5)	0.3150(7)	0.051(3)	C28	−0.315(1)	0.5032(7)	0.108(1)	0.093(6)
C8	0.1985(8)	0.1218(6)	0.2860(7)	0.058(3)	C29	−0.074(1)	0.5188(7)	0.158(1)	0.094(6)
C9	0.229(1)	0.1016(7)	0.4206(9)	0.080(5)	C30	−0.2685(9)	0.2393(7)	−0.1191(8)	0.082(4)
C10	0.0624(9)	0.0933(7)	0.2127(9)	0.079(5)	C31	−0.407(1)	0.208(1)	−0.170(1)	0.133(7)
C11	0.297(1)	0.0704(6)	0.251(1)	0.081(5)	C32	−0.175(1)	0.1695(9)	−0.1186(9)	0.109(6)
C12	0.2396(9)	0.3271(7)	−0.0223(7)	0.069(4)	C33	−0.255(2)	0.316(1)	−0.1942(9)	0.155(9)
C13	0.148(2)	0.401(1)	−0.072(1)	0.141(8)	C34	−0.2661(9)	0.1624(7)	0.2909(9)	0.078(5)
C14	0.369(1)	0.351(1)	−0.0244(9)	0.148(9)	C35	−0.3627(9)	0.2090(8)	0.332(1)	0.087(5)
C15	0.181(2)	0.2551(9)	−0.1053(9)	0.135(8)	C36	−0.158(1)	0.1234(8)	0.399(1)	0.102(6)
C16	0.3988(9)	0.4249(7)	0.4040(8)	0.074(4)	C37	−0.340(1)	0.0880(7)	0.212(1)	0.109(7)

[a] Numbers in parentheses are estimated standard deviations.

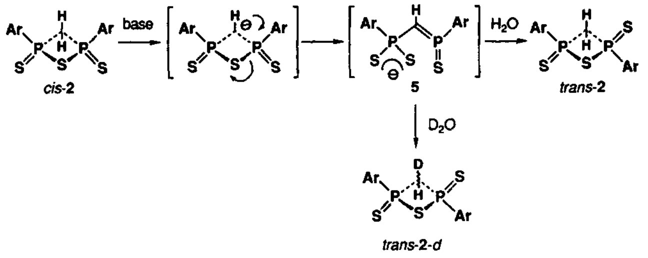
[b] Equivalent isotropic *U* is defined as one-third the trace of the orthogonalized U_{ij} tensor.

3-^{18}O in toluene in the presence of DBU and $H_2{}^{18}O$ did not take place.

To examine the possibility that *cis*-**3** was formed from the further reaction of the accompanying products (i.e., *cis*- and *trans*-**2** and *trans*-**4**) with water, the following experiments were carried out. Attempted reaction of *trans*-**2** with water in 1,4-dioxane in the presence of DBU for 21 hours at room temperature resulted in the recovery of the starting *trans*-**2**. The dithiadiphospholane *trans*-**4** was desulfurized [9] in 1,4-dioxane in the presence of DBU and water at room temperature to give *cis*-**2**; however, the formation of *cis*-**3** was not observed during this reaction. Attempted conversion of *cis*-**2** to *cis*-**3** in 1,4-dioxane in the presence of DBU and water for 24 hours at room temperature has also been unsuccessful.

These results indicate that the oxygen atom of *cis*-**3** has been introduced during the sulfurization process, probably by the reaction of some intermediary species with water.

During the mechanistic study described previously, we have found the isomerization of *cis*-**2** to *trans*-**2**. Both *cis*-**2** and *trans*-**2** remained almost unchanged, even in refluxing toluene for 18 hours in the absence of a base. However, the isomerization of *cis*-**2** took place quite fast in refluxing toluene in the presence of DBU to give *trans*-**2** almost quantitatively. Even at room temperature, the isomerization of *cis*-**2** in the presence of DBU proceeded slowly; thus, *trans*-**2** was obtained in 80% yield together with 9% recovery of *cis*-**2** after 93 hours of stirring. In the presence of a weaker base, such as triethylamine, the isomerization was slow



SCHEME 2

and a 79% yield of *trans*-**2** was obtained after 72 hours of refluxing in triethylamine together with a 16% recovery of *cis*-**2**. On the other hand, attempted isomerization of *trans*-**2** resulted in the recovery of the starting material either after 6 hours of refluxing in toluene in the presence of DBU (98% recovery of *trans*-**2**) or after 24 hours of refluxing in the absence of DBU (82% recovery of *trans*-**2**).

To obtain insight into the reaction mechanism of isomerization, we attempted the isomerization reaction in the presence of D_2O. The ^{1}H NMR spectrum of the product, *trans*-**2**, indicated that the deuterium was incorporated into the methylene group of the four-membered ring, suggesting the following mechanism. Proton abstraction with bases occurs at the 3-position of the thiadiphosphetane ring, resulting in bond cleavage of one of the P–S bonds to give an intermediate **5** carrying both phosphaethylene *P*-sulfide moiety and phosphinodithioate group. The intermediate thus formed then cyclizes back to thiadiphosphetane disulfide of the *trans* configuration, because the *trans* isomer might be thermodynamically more favorable than the *cis* isomer. This type of intermediate is plausible to be operative, because similar hypervalent phosphorus compounds have been reported during the sulfurization reactions of phosphaalkenes, phosphaallenes, or diphosphenes [15].

Attempted photoisomerization of *cis*- or *trans*-**2** by use of a medium-pressure mercury lamp in toluene at room temperature for 1 hour resulted in the recovery of the starting material. This indicates that inversion at either of the phosphorus atoms does not take place on irradiation. It should be noted that attempted isomerization of *cis*-**3** by heating in toluene in the presence of DBU resulted in decomposition to an unidentified complex mixture.

Taking into account the above results on isomerization or desulfurization, Scheme 3 shows a possible mechanism of the sulfurization reaction of **1**. An unstable intermediate, such as **6**, is first formed, which may be converted into *cis*-**3** and *trans*-**4** by moisture. *Trans*-**4** is easily desulfurized by DBU to give *cis*-**2** as a major product [16], and *cis*-**2** is isomerized to *trans*-**2** by DBU only very slowly at room temperature.

We have observed some intermediary ^{31}P NMR signals around $\delta_P = 100$ at the early stage of the sulfurization reaction. However, attempted isolation or characterization of the intermediary species has been unsuccessful because of their instability.

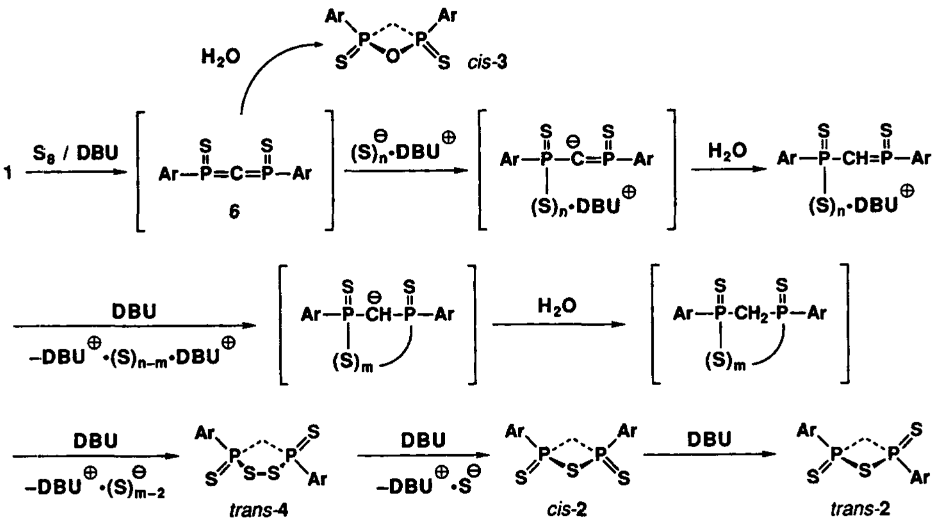
EXPERIMENTAL

*Preparation of cis-2,4-bis(2,4,6-tri-t-butylphenyl)-1,2,4-oxadiphosphetane 2,4-disulfide (cis-*3*)*

To a solution of the diphosphaallene **1** (158.1 mg, 0.28 mmol) and elemental sulfur (31.9 mg, 1.0 mg-atom) in toluene (6 mL) was added 25 μL (0.17 mmol) of DBU *via* a syringe. The mixture changed gradually to red, and the solution was stirred at room temperature for 25 hours. Removal of the solvent followed by chromatographic separation (SiO_2/CCl_4-$CHCl_3$) afforded *cis*-**3** (yield 13%) together with *cis*-2,4-bis(2,4,6-tri-*t*-butylphenyl)-1,2,4-thiadiphosphetane 2,4-disulfide (*cis*-**2**) in 36% yield, *trans*-3,5-bis(2,4,6-tri-*t*-butylphenyl)-1,2,3,5-dithiadiphospholane 3,5-disulfide (*trans*-**4**) in 12% yield, and *trans*-2,4-bis(2,4,6-tri-*t*-butylphenyl)-1,2,4-thiadiphosphetane 2,4-disulfide (*trans*-**2**) in 3% yield.

cis-**3**: Mp 268–270°C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.11 (4H, bs, arom.), 4.25 (1H, pseudo q, $^2J_{PH}$ = 13.6 Hz, $^2J_{HH}$ = 14.0 Hz, PCHP), 4.11 (1H, dt, $^2J_{PH}$ = 9.9 Hz, $^2J_{HH}$ = 14.5 Hz, PCHP), 1.49 (18H, s, *o*-Bu^t), 1.42 (18H, s, *o*′-Bu^t), and 1.24 (18H, s, *p*-Bu^t); ^{31}P{^{1}H} NMR (81 MHz, $CDCl_3$) δ 89.8; ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 155.8 (pseudo t, J_{PC} = 2.5 Hz, *o*-arom.), 153.5 (t, J_{PC} = 12.6 Hz, *o*′-arom.), 151.8 (s, *p*-arom.), 130.9 (dd, $^1J_{PC}$ = 105.5 Hz, $^3J_{PC}$ = 7.3 Hz, *ipso*-arom.), 123.8 (t, J_{PC} = 6.6 Hz, *m*-arom.), 123.5 (t, J_{PC} = 7.7 Hz, *m*′-arom.), 70.4 (t, $^1J_{PC}$ = 48.6 Hz, P$\underline{\mathrm{C}}$P), 40.5 (s, *o*-$\underline{\mathrm{C}}\mathrm{Me}_3$), 40.0 (s, *o*′-$\underline{\mathrm{C}}\mathrm{Me}_3$), 34.8 (s, *p*-$\underline{\mathrm{C}}\mathrm{Me}_3$), 34.1 (s, *o*-$\mathrm{C}\underline{\mathrm{Me}}_3$), 33.8 (s, *o*′-$\mathrm{C}\underline{\mathrm{Me}}_3$), 31.0 (s, *p*-$\mathrm{C}\underline{\mathrm{Me}}_3$); UV ($CH_2Cl_2$) λ_{max} 248 (log ϵ 4.4) and *ca.* 304 nm (sh, 3.6); IR (KBr) 820 and 734 cm^{-1}; MS *m/z* (rel intensity) 646 (M^+; 1) and 589 (M^+-Bu^t; 100); FDMS *m/z* 646; Found: *m/z* 589.2851; Calcd for $C_{33}H_{51}OP_2S_2$: M-Bu^t 589.2857.

cis-**2**: Mp 234–236°C; ^{1}H NMR ($CDCl_3$) δ 7.11 (2H, s, arom.), 7.08 (2H, d, $^4J_{PH}$ = 4.7 Hz, arom.), 4.52 (1H, dt, $^2J_{PH}$ = 11.3 Hz, $^2J_{HH}$ = 13.7 Hz, PCHP), 4.20 (1H, pseudo q, $^2J_{PH}$ = $^2J_{HH}$ = 12.8 Hz, PCHP), 1.47 (18H, s, *o*-Bu^t), 1.46 (18H, s, *o*′-Bu^t), and 1.21 (18H, s, *p*-Bu^t); ^{31}P{^{1}H} NMR ($CDCl_3$) δ 48.1; ^{13}C{^{1}H} NMR ($CDCl_3$) δ 156.9 (bs, *o*-arom.), 153.1 (d, $^2J_{PC}$ = 10.8 Hz, *o*′-arom.), 151.9 (pseudo t, J_{PC} = 1.8 Hz, *p*-arom.), 134.9 (dd, $^1J_{PC}$ = 78.6 Hz, $^3J_{PC}$ = 5.3 Hz, *ipso*-arom.), 124.5 (d, $^3J_{PC}$ = 14.7 Hz, *m*-arom.), 123.2 (d, $^3J_{PC}$ = 15.2 Hz, *m*′-arom.), 71.7 (t, $^1J_{PC}$ = 47.3 Hz, P$\underline{\mathrm{C}}$P), 41.2 (s, *o*-$\underline{\mathrm{C}}\mathrm{Me}_3$), 40.3 (s, *o*′-$\underline{\mathrm{C}}\mathrm{Me}_3$), 34.6 (s,



SCHEME 3

p-$\underline{C}$Me$_3$), 34.5 (s, *o*-C$\underline{Me_3}$), 34.4 (s, *o*′-C$\underline{Me_3}$), 30.9 (s, *p*-C$\underline{Me_3}$), UV (CH$_2$Cl$_2$) λ_{max} 266 nm (log ε 4.3); IR (KBr) 782 and 762 cm^{-1}; MS *m/z* (rel intensity) 662 (M$^+$; 1) and 605 (M$^+$-Bu^t; 100); FDMS *m/z* 662; Found: *m/z* 605.2626; Calcd for C$_{33}$H$_{51}$P$_2$S$_3$: M-Bu^t 605.2628.

trans-**4**: Mp 208–210°C (decomp); ^{1}H NMR (CDCl$_3$) δ 7.25 (4H, bs, arom.), 3.96 (2H, t, $^2J_{PH}$ = 9.6 Hz, PCH$_2$P), 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 (CDCl$_3$) δ 87.6; ^{13}C {^{1}H} NMR (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, P$\underline{C}$P), 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$\underline{Me_3}$); UV (CH$_2$Cl$_2$) λ_{max} 261 (log ε 4.3) and *ca.* 321 nm (sh, 3.8); 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$_2$S$_4$: 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$_2$P), 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, P$\underline{C}$P), 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$\underline{Me_3}$); UV (CH$_2$Cl$_2$) λ_{max} *ca.* 274 nm (sh, log ε 4.1); 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$_2$S$_3$: M, 662.3332.

Sulfurization of 1,3-Bis(2,4,6-tri-t-butylphenyl)-1,3-diphosphaallene (**1**) *in Triethylamine at Higher Temperature*

A solution of **1** (327.1 mg, 0.58 mmol) and elemental sulfur (67.3 mg, 2.1 mg-atom) in triethylamine (20 mL) was stirred at 70°C for 9 hours. Removal of the solvent in vacuo followed by chromatographic separation afforded *cis*-**2** (17%), *trans*-**2** (1%), *cis*-**3** (3%), and *trans*-**4** (4%).

Sulfurization of **1** *in the Presence of $H_2{}^{18}O$*

To a solution of the diphosphaallene **1** (100 mg, 0.17 mmol) and elemental sulfur (19.7 mg, 0.61 mg-atom) in dry toluene (3.8 mL) were added 7 μL of H$_2{}^{18}$O (0.4 mmol; ^{18}O content: 80.3 at. %) and 16 μL (0.11 mmol) of DBU *via* a syringe. The mixture was stirred at room temperature for 24 hours. Removal of the solvent followed by chromatographic separation afforded a mixture of *cis*-**3** and *cis*-**3**-^{18}*O* in 32% yield together with *cis*-**2** in 12% yield. By comparison of an MS spectrum of the mixture (*cis*-**3** and *cis*-**3**-^{18}*O*) with the spectrum of pure *cis*-**3**, the ^{18}O content was determined to be 63%.

*Attempted Reaction of cis-**3** with $H_2{}^{18}O$*

A mixture of *cis*-**3** (12 mg, 0.020 mmol), H$_2{}^{18}$O (3 μL, 0.15 mmol), and DBU (7 μL, 0.047 mmol) in toluene (1.5 mL) was stirred at room temperature for 24 hours. The MS spectrum of the recovered *cis*-**3** (78% recovery) indicated that ^{18}O was not incorporated under the reaction conditions.

Attempted Reaction of *trans*-**2** with Water

To a solution of *trans*-**2** (39.8 mg, 0.060 mmol) in 1,4-dioxane (10 mL) were added 1.0 mL (56 mmol) of water and 9 μL (0.06 mmol) of DBU. The solution was stirred for 21 hours at room temperature. The ^{31}P NMR spectrum of the resulting solution showed a single peak due to the starting *trans*-**2**. After chromatographic separation, 37.0 mg (93%) of *trans*-**2** was recovered.

Desulfurization of *trans*-**4** in the Presence of DBU and Water

A 1,4-dioxane (8.0 mL) solution of *trans*-**4** (17.0 mg, 0.024 mmol), water (0.4 mL, 22 mmol), and DBU (4 μL, 0.027 mmol) was stirred for 4 days at room temperature. Signals due to *trans*-**4** and the desulfurized products *cis*-**2** and *trans*-**2** were observed by ^{31}P NMR spectroscopy (*trans*-**4**:*cis*-**2**:*trans*-**2** = 20:1:1); however, a signal due to *cis*-**3** was not observed.

Attempted Reaction of *cis*-**2** with Water

To a solution of *cis*-**2** (24.0 mg, 0.036 mmol) in 1,4-dioxane (5 mL) were added 0.5 mL (28 mmol) of water and 4.5 μL (0.03 mmol) of DBU. The solution was stirred for 24 hours at room temperature. The ^{31}P NMR spectrum of the resulting solution showed a single peak due to the starting *cis*-**2**. After chromatographic separation, 21.7 mg (90%) of *cis*-**2** was recovered.

Base-Induced Isomerization of *cis*-**2**

To a solution of *cis*-**2** (40.6 mg; 0.061 mmol) in toluene (2 mL) was added 9 μL (0.06 mmol) of DBU, and the mixture was refluxed for 6 hours. Then, the solvent was removed in vacuo, and the ^{1}H and the ^{31}P NMR investigation of the residue indicated the quantitative conversion to the *trans* isomer (>99%). Chromatographic separation afforded 40.4 mg (99.5% yield) of *trans*-**2**. The *cis* isomer was not recovered.

Attempted Isomerization of *cis*-**2** in the Absence of DBU

Toluene (2.5 mL) solution of *cis*-**2** (41.8 mg, 0.063 mmol) was heated to reflux for 24 hours. The ^{31}P NMR spectrum of the resulting solution showed only a single peak due to *cis*-**2**. By silica-gel column chromatography, 38.5 mg (92%) of *cis*-**2** was recovered.

Isomerization of *cis*-**2** at Room Temperature

To a solution of *cis*-**2** (39.8 mg, 0.060 mmol) in toluene (2 mL) was added 9 μL (0.06 mmol) of DBU, and the mixture was stirred for 93 hours at room temperature. Removal of the solvent in vacuo followed by chromatographic separation afforded *trans*-**2** in 80% yield and *cis*-**2** in 9% recovery.

Isomerization of *cis*-**2** in Triethylamine

A solution of *cis*-**2** (39.9 mg, 0.060 mmol) in triethylamine (8 mL) was refluxed for 72 hours. Then, the solvent was evaporated, and the residue was chromatographed to give *trans*-**2** in 79% yield and *cis*-**2** in 16% recovery.

Isomerization of *cis*-**2** in the Presence of D_2O

To a solution of *cis*-**2** (66.3 mg, 0.10 mmol) in dry tetrahydrofuran (16 mL) were added 37 μL of D_2O (deuterium content: 99.8%) and 74 μL (0.51 mmol) of DBU. The mixture was heated to reflux for 6 hours. Removal of the solvent in vacuo followed by chromatographic separation afforded 53.5 mg of *trans*-**2**. The ^{1}H NMR spectrum of the product indicated that deuterium was incorporated at the methylene group of the thiadiphosphetane ring. The deuterium content was determined to be about 70% based on the integral of the signals.

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

The compound *cis*-**3** was recrystallized from toluene/hexane. *Crystal data*: $C_{37}H_{60}OP_2S_2$, $M = 646.96$, monoclinic, space group $P2_1$, $a = 11.211(1)$, $b = 15.754(3)$, $c = 11.978(1)$ Å, $\beta = 111.00(1)°$, $U = 1975.2(5)$ Å^3, $Z = 2$, $D_c = 1.088$ g cm^{-3}, and $\mu = 21.52$ cm^{-1}. A total of 2880 reflections with $2\theta \leq 120°$ were recorded on a four-circle diffractometer using graphite-monochromated Cu-K_α radiation. Of these, 2615 [with $I > 3\sigma(I)$] were judged as observed. The structure was solved using SHELX86 [17]. All hydrogen atoms could be located on a difference Fourier synthesis. Full-matrix least-squares refinement with anisotropic temperature factors for nonhydrogen atoms converged to $R = 0.053$ and $R_w = 0.054$ [18].

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SUPPLEMENTARY MATERIAL AVAILABLE

Tables of atomic coordinates, anisotropic thermal parameters, H-atom coordinates, bond distances and angles, and structure factors for *cis*-**3** (13 pages) are available on request from the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2, 1EW, United Kingdom.

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[16] It should be noted that the desulfurization of *trans*-**4** did not take place without DBU in refluxing toluene for 1 hour. Attempted preparation of *trans*-**4** by sulfurization reaction of *cis*-**2** or *cis*-**3** in the presence of DBU did not proceed either.

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