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Persulfuration of Phosphinines: Synthesis and X-ray Crystal Structure Analysis of a P_2S_3 Derivative

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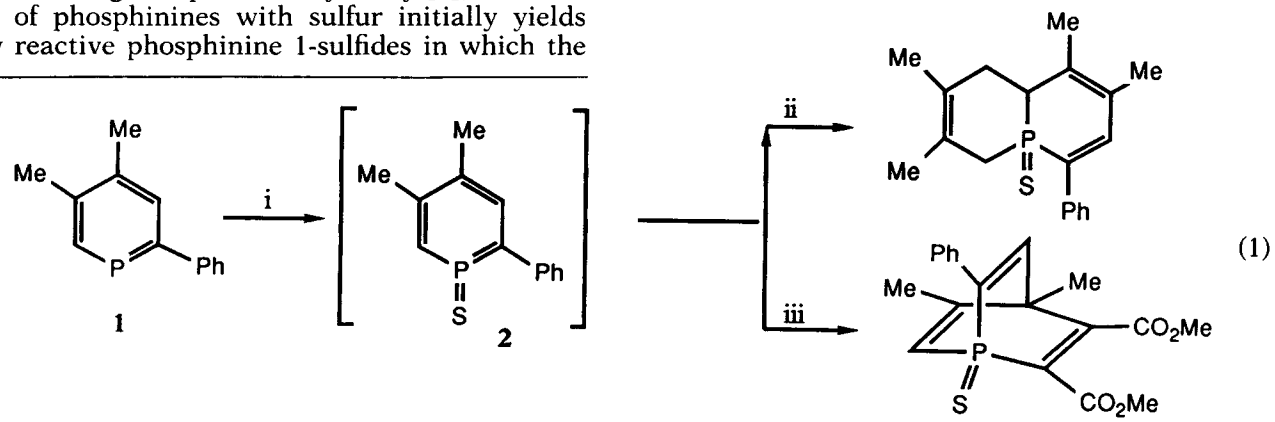
ABSTRACT

The reaction of 4,5-dimethyl-2-phenylphosphinine with sulfur in boiling benzene in the presence of N-methylimidazole as a catalyst first yields a P-sulfide. This monosulfide further reacts with sulfur to give a diphosphinine trisulfide and a diphosphinine tetrasulfide. The X-ray crystal structure analysis of the trisulfide has been carried out.

The two head-to-tail 1,6-dihydrophosphinine rings are connected by P–S–C and P–C links, thus forming a central 1,2,4-thiadiphospholane heterocycle. The P–C bridge is weak [1.881(3) Å] and sulfur can insert into it to give the symmetrical tetrasulfide with two P–S–C bridges.

According to a preliminary study [1], the reaction of phosphinines with sulfur initially yields very reactive phosphinine 1-sulfides in which the aromaticity of the ring appears to have been lost. Since our initial report, phosphinine 1-sulfides have been generated by thermal decomposition of 1-phospha-2-thiabicyclo[4.4.0]deca-3,7,9-triene 1-sulfides [2] and a stable example has been reported [3]. In view of the aromaticity loss that accompanies the sulfuration of phosphorus, it seemed to us that the reaction of phosphinines with sulfur deserved more attention. We therefore decided to investigate in more depth the reaction of 4,5-dimethyl-2-phenylphosphinine (**1**) with sulfur.

In our initial report, phosphinine **1** ($\delta^{31}P$ + 185) was allowed to react with sulfur in boiling xylene. A signal at δ + 145.7 appeared on the ^{31}P NMR spectrum of the crude reaction mixture which was assigned to the phosphinine sulfide **2** on the basis of trapping reactions with 2,3-dimethylbutadiene and dimethyl acetylenedicarboxylate (Eq. 1).



(1)

i, S_8, xylene, reflux; ii, dimethylbutadiene; iii, dimethylacetylene dicarboxylate

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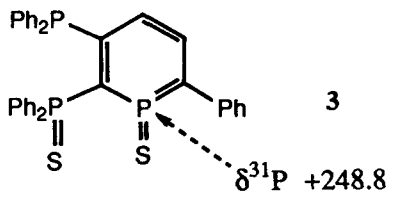

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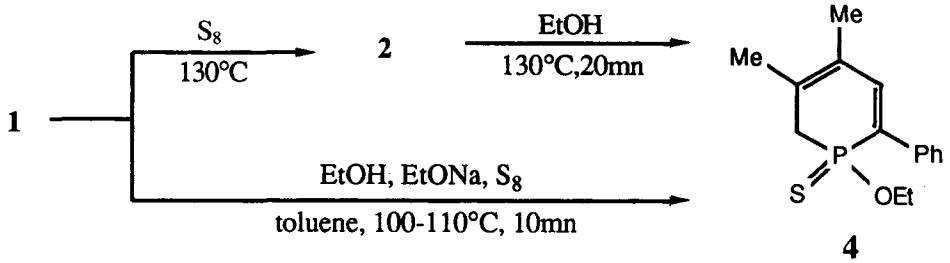
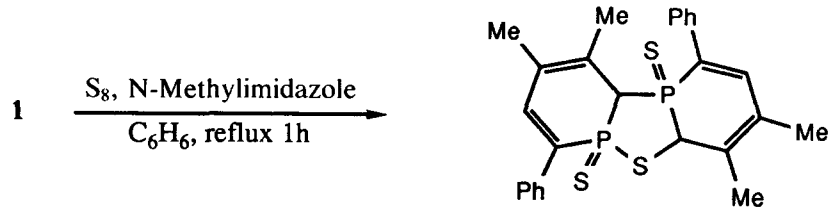
Soon after this report was published, a stable phosphaalkene sulfide was described by Nielson [4] with a chemical shift of +190.9, which supports our assignment. It must be stressed here that the very low-field shift observed for the stable phosphinine sulfide **3** [3] may be due to the polarization of the P=C double bond by the $P(S)Ph_2$ electron-attracting substituent.

An additional confirmation of the structure of **2** was obtained by allowing it to react with ethanol. An almost quantitative reaction was observed which led to the expected adduct **4** [5] (Eq. 2).



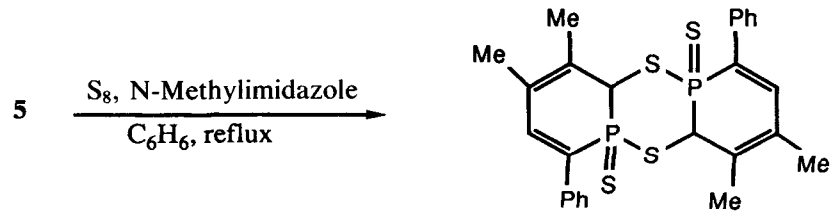
4 (2)

The same adduct was directly obtained from phosphinine **1**, sulfur, and ethanol in the presence of catalytic amounts of EtONa (Eq. 2). More interesting was the discovery that, in the presence of *N*-methylimidazole as a catalyst, the reaction of **1** with sulfur proceeds further to give a new product **5**, with two different phosphorus atoms (Eq. 3).



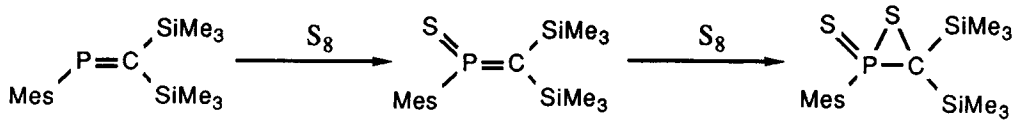
5 (3)

The mass spectrum of **5** shows a molecular peak at *m/z* 496. Thus, **5** results from the addition of three sulfur atoms onto two molecules of phosphinine. The structure of **5** was established by X-ray crystal structure analysis (Fig. 1). Bond distances and bond angles are given in Tables 1 and 2. The P···S single- and double-bond lengths in **5** are absolutely normal. The comparison with the structure of the five-membered heterocycle $\overline{S—CH_2—CH_2—S—P(S)Ph}$ is illustrative: P=S 1.936 Å, P—S 2.087 Å [6]. In contrast, the P_7C_6 bond within the central five-membered ring of **5** appears to be extremely weak: 1.881(3) Å. This bond is easily cleaved by sulfur. Indeed, upon further sulfuration, the "diphosphinine trisulfide" **5** is transformed into the "diphosphinine tetrasulfide" **6** (Eq. 4).



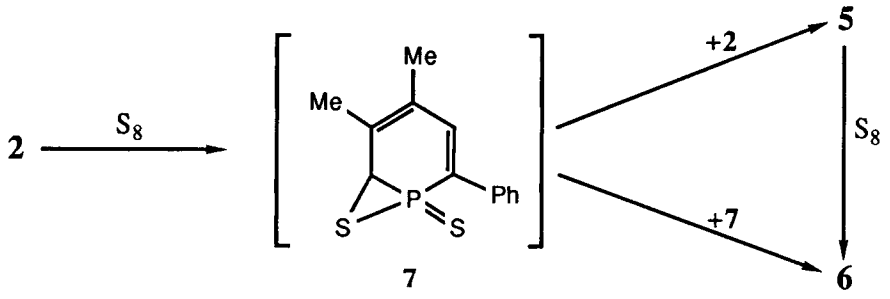
6 (4)

The symmetrical tetrasulfide gives only one ^{31}P resonance at δ + 67.7. Its mass spectrum shows a molecular peak at m/z 528. The ^{1}H and ^{13}C NMR spectra clearly indicate the presence of two identical 1,2-dihydrophosphinine rings. Neilson [4] has shown that sulfur reacts with a phosphaalkene to give first a monosulfide and then a disulfide (Eq. 5).



(5)

Since the phosphinine monosulfide **2** appears to have the same reactivity as a "normal" phosphaalkene P sulfide, we suspect that the first step of the persulfuration of phosphinine **1** is the formation of a transient disulfide **7.** It would then react with a molecule of monosulfide **2** to give the diphosphinine trisulfide **5** or would dimerize to give the diphosphinine tetrasulfide **6** (Eq. 6).



(6)

From this series of results, it clearly appears that the courses of the reactions of phosphinines with oxygen [7] and sulfur are very different even though, in both cases, a *P*-monoxide and a *P*-monosulfide are probably formed in the first steps. In the case of oxygen, further reaction yields 1,2- and 1,4-dihydrophosphinine oxides [7].

EXPERIMENTAL

Nuclear magnetic resonance spectra (chemical shifts in parts per million from internal Me_4Si for ^{1}H and ^{13}C and from external H_3PO_4 for $^{31}P\{^{1}H\}$; positive for downfield shifts in all cases) were recorded on a Bruker WP80 instrument, respectively, at 80.13, 20.15, and 32.44 MHz. Mass spectra (electronic impact, EI) were recorded on a Shimadzu QP1000 spectrometer. All reactions were carried out under argon. Chromatographic separations were performed on deoxygenated silica gel columns (70-230 mesh, Riedel de Haën).

4,5-Dimethyl-2-phenylphosphinine 1-sulfide (**2**)

One gram (5 mmol) of the phosphinine **1** and 0.19 g (0.75 mmol) of S_8 were heated 20 min in a sealed tube at 130°C. After cooling, dry toluene was added.

FIGURE 1 ORTEP drawing of one molecule of the "diphosphinine trisulfide" **5.** Vibrational ellipsoids are scaled to enclose 50% of the electron density. Hydrogen atoms are omitted for clarity.

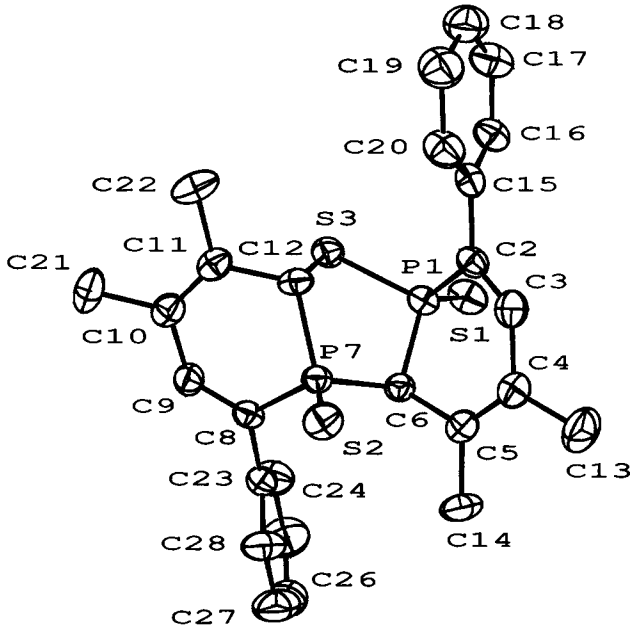


TABLE 1 "Diphosphinine Trisulfide" **5**: Selected Bond Distances

Atom 1	*Atom 2*	*Distance (Å)*[a]	*Atom 1*	*Atom 2*	*Distance (Å)*[a]
S1	P1	1.932(1)	S3	C12	1.838(3)
S2	P7	1.938(1)	S3	P1	2.071(1)
P1	C2	1.798(3)	P1	C6	1.829(2)
P7	C6	1.881(3)	P7	C8	1.798(3)
P7	C12	1.834(2)	C2	C3	1.334(3)
C3	C4	1.467(4)	C4	C5	1.342(5)
C5	C6	1.502(4)	C8	C9	1.339(4)
C9	C10	1.462(4)	C10	C11	1.341(5)
C11	C12	1.516(4)			

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

The ^{31}P NMR spectrum showed a major signal at 145.5 ppm, corresponding to the sulfide **2**, and a minor signal at 184.5 ppm, corresponding to some unreacted starting material.

1-Ethoxy-4,5-dimethyl-2-phenyl-1 phosphacyclohexa-2,4-diene 1-sulfide (**4**)

Method A A mixture of 1.0 g (5 mmol) of phosphinine **1**, 0.2 g (0.8 mmol) of S_8 and a catalytic amount of EtONa in 15 mL of toluene and 5 mL of dry EtOH was heated 10 min at 100–110°C. After vacuum distillation of the solvents, the residue was chromatographed with toluene, leading to 1.0 g (yield 71.9%) of a pale yellow solid, mp 93°C.

Phosphorus-31 NMR ($CDCl_3$) δ74.8; Hydrogen-1 NMR ($CDCl_3$) δ1.17 (*t*, $^3J_{HH}$ 6.9 Hz, 3*H*, CH_3), 1.88, and 1.91 (6*H*, = C–*Me*); 3.05 (*m*, $^2J_{HP}$ 24.2 Hz, 2*H*, CH_2P); 4.02 (*m*, $^3J_{HH}$ 6.85 Hz, 2*H*, OCH_2); 6.52 (*d*, $^3J_{HP}$ 37.1 Hz, 1*H*, =CH); 7.25–7.67 (*m*, 5*H*, aromatic); Carbon-13 NMR ($CDCl_3$) δ16.4 (*d*, $^3J_{CP}$ 6.1 Hz, CH_3); 19.3 (*d*, $^3J_{CP}$ 2.4 Hz, C_5–CH_3); 21.9 (*d*, $^4J_{CP}$ 9.0 Hz, C_4–CH_3); 41.9 (*d*, $^1J_{CP}$ 75.7 Hz, C_6); 61.2 (*d*, $^2J_{CP}$ 6.1 Hz, OCH_2); 125.6 (*d*, $^1J_{CP}$ 17.1 Hz, C_2); 127.1–128.1 (*m*, aromatic CH); 129.3 (*d*, J_{CP} 9.8 Hz), 134.2 (*s*) and 136.5 (*d*, J_{CP} 7.3 Hz; C_4, C_5, and ipso-C); 141.3 (*d*, $^2J_{CP}$ 6.1 Hz, C_3); Mass spectrum (70 eV) *m/z* (relative intensity) 278 (M, 100), 245 (M–SH, 30), 232 (M–EtOH, 40), 170 (M–Ph–S + 1, 90); analysis calculated for $C_{15}H_{19}OPS$: C, 64.74; H, 6.83; P, 11.15; S, 11.51. Found: C, 64.51; H, 6.85; P, 11.05; S, 11.47.

Method B To the toluene solution of the phosphinine sulfide **2** (obtained from 5 mmol of phosphinine **1** as described) was added 5 mL of dry ethanol and the mixture was warmed 20 min at 130°C in a sealed tube. The ^{31}P NMR spectra showed a major signal at δ + 77.0 (ethoxy compound **4**) and two minor signals at 184.6 (phosphinine **1**) and 67.2 (sulfide **6**).

4,5,10,11-Tetramethyl-7,13-diphenyl-2-thia-1,8-diphosphatricyclo[7.4.0.0^{3,8}]trideca-4,6,10,12-tetraene 1,8-disulfide (**5**)

A mixture of 2 g (10 mmol) of phosphinine **1**, 0.53 g (2.0 mmol) of S_8 and 15 drops of *N*-methylimida-

TABLE 2 "Diphosphinine Trisulfide" **5**: Selected Bond Angles

Atom 1	*Atom 2*	*Atom 3*	*Angle (°)*[a]	*Atom 1*	*Atom 2*	*Atom 3*	*Angle (°)*[a]
P1	S3	C12	94.92(9)	C2	C3	C4	127.9(3)
S1	P1	S3	112.24(4)	C3	C4	C5	122.7(3)
S1	P1	C2	116.4(1)	C4	C5	C6	120.7(2)
S1	P1	C6	117.8(1)	P1	C6	P7	108.0(1)
S3	P1	C2	106.74(9)	P1	C6	C5	113.4(2)
S3	P1	C6	101.3(1)	P7	C6	C5	113.8(2)
C2	P1	C6	100.6(1)	P7	C8	C9	118.7(2)
S2	P7	C6	114.55(9)	C8	C9	C10	127.7(3)
S2	P7	C8	116.60(9)	C9	C10	C11	122.8(3)
S2	P7	C12	114.6(1)	C10	C11	C12	121.2(3)
C6	P7	C8	105.1(1)	S3	C12	P7	108.5(2)
C6	P7	C12	103.8(1)	S3	C12	C11	106.2(2)
C8	P7	C12	100.4(1)	P7	C12	C11	114.7(2)
P1	C2	C3	116.3(2)				

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

Table of Positional Parameters and Their Estimated Standard Deviations

Atom[a]	x	y	z	B (A2)
S1	0.66646(5)	0.26978(8)	0.60871(6)	4.64(2)
S2	0.84009(5)	−0.17990(8)	0.86670(5)	4.03(2)
S3	0.62341(5)	−0.02563(8)	0.58078(5)	3.83(2)
P1	0.67933(5)	0.11705(7)	0.67213(5)	3.13(1)
P7	0.79202(4)	−0.10879(7)	0.74393(4)	2.83(1)
C2	0.6308(2)	0.1092(3)	0.7549(2)	3.14(6)
C3	0.6893(2)	0.1271(3)	0.8434(2)	3.71(7)
C4	0.7894(2)	0.1481(3)	0.8823(2)	3.79(7)
C5	0.8406(2)	0.1172(3)	0.8375(2)	3.53(7)
C6	0.7964(2)	0.0614(3)	0.7426(2)	3.09(6)
C8	0.8446(2)	−0.1573(3)	0.6701(2)	3.07(6)
C9	0.8029(2)	−0.2442(3)	0.6074(2)	3.52(6)
C10	0.7158(2)	−0.3056(3)	0.5887(2)	3.62(7)
C11	0.6546(2)	−0.2632(3)	0.6183(2)	3.65(7)
C12	0.6704(2)	−0.1439(3)	0.6699(2)	3.35(6)
C13	0.8321(3)	0.2047(4)	0.9774(2)	6.2(1)
C14	0.9439(2)	0.1316(4)	0.8774(2)	4.89(8)
C15	0.5304(2)	0.0838(3)	0.7219(2)	3.24(6)
C16	0.4630(2)	0.1583(3)	0.6579(2)	3.94(7)
C17	0.3705(2)	0.1339(4)	0.6305(2)	4.98(8)
C18	0.3434(2)	0.0341(4)	0.6635(2)	5.52(9)
C19	0.4091(2)	−0.0426(3)	0.7255(3)	5.60(9)
C20	0.5024(2)	−0.0169(3)	0.7551(2)	4.54(7)
C21	0.6972(3)	−0.4185(3)	0.5295(2)	5.23(9)
C22	0.5631(2)	−0.3212(4)	0.5982(3)	5.62(9)
C23	0.9341(2)	−0.1018(3)	0.6825(2)	3.50(6)
C24	0.9381(2)	−0.253(4)	0.6158(2)	5.40(9)
C25	1.0216(3)	0.0278(4)	0.6286(3)	7.2(1)
C26	1.0999(2)	0.0039(4)	0.7052(3)	6.6(1)
C27	1.0971(2)	−0.0720(5)	0.7714(3)	6.7(1)
C28	1.0147(2)	−0.1254(4)	0.7610(2)	5.25(9)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: (4/3)* [a2*B(1,1) + b2*B(2,2) + c2*B(3,3) + ab(cos γ)*B(1,2) + ac(cos β)*B(1,3) + bc(cos α)*B(2,3)].

zole in 10 mL dry benzene was heated 1 h at reflux. The solvent was evaporated and the residue chromatographed with toluene. Yield, 1.2 g (48.4%) of a pale yellow solid; mp 250°C (decomp.). Phosphorus-31 NMR ($CDCl_3$) δ46.1 and 46.7 (central peaks of the *AB* system; side peaks have not been detected).

Hydrogen-1 NMR ($CDCl_3$) 1.53 (*d*, $^4J_{HP}$ 4.3 Hz, 3*H*, C_4–CH_3); 1.70 (*s*, 3*H*, C_5–CH_3); 1.88 (*s*, 3*H*, C_{11}–CH_3); 2.0 (badly resolved *q*, $^4J_{HP}$ 5.2 and 6.3 Hz, 3*H*, C_{10}–CH_3); 3.37 (*q*, $^2J_{HP}$ 14.2 and 16.9, 1*H*, H_9); 3.49 (*d*, $^2J_{HP}$ 4.8 Hz, 1*H*, H_3); 6.47 (*d*, $^3J_{HP}$ 35.3 Hz) and 6.70 (*d*, $^3J_{HP}$ 38.0 Hz, 2*H*, H_6 and H_{12}); 7.38–7.44, 7.59–7.64; and 7.70–7.75 (*m*, 10*H*, Ph). Carbon-13 NMR ($CDCl_3$) δ19.5 and 19.8 (*m*), 21.2 (*d*, J_{CP} 7.3 Hz) and 22.0 (weakly resolved *q*, J_{CP} 2.4 and 9.7 Hz; Me); 51.3 (*q*, $^1J_{CP}$ 34.2 and 39.0 Hz, C_3); 54.9 (poorly resolved *q*, $^1J_{CP}$ ca. 44.0 Hz and 45.0 Hz, C_9); 124.9 and 125.3 (two pseudo *t*, C_7 and C_{13}), 126.7 (*s*) and 128.4–128.9 (*m*, aromatic CH); 131.4 (*m*), 134.8 (*d*, J_{CP} 8.5 Hz) and 136.4 (*d*, J_{CP} 8.5 Hz; C_4, C_5, C_{10}, C_{11} and C-ipso); 139.4 (*d*, $^2J_{CP}$ 4.9 Hz; C_6); 143.7 (pseudo *t*, C_{12}). Mass spectrum (70 eV *m/z* (relative intensity); 496 (M, 10), 232 [(M–S/2, 100], 200 [(M–2S/2, 50]. Analysis calculated for $C_{26}H_{26}P_2S_3$: C, 62.90; H, 5.24; P, 12.50; S, 19.35. Found: C, 62.84; H, 5.24; P, 12.63; S, 19.10.

4,5,11,12-Tetramethyl-7,14-diphenyl-2,9-dithia-1,8-diphosphatricyclo[8.4.0.0^{3,8}] tetradeca-4,6,11,13-tetraene 1,8-disulfide (**6**)

A mixture of 2 g (10 mmol) of phosphinine **1**, 0.96 g (3.75 mmol) of S_8 and 15 drops of *N*-methylimidazole in 20 mL of benzene was heated 1 h at reflux. The reaction mixture was chromatographed first with hexane and then with toluene, leading to 1.60 g (yield 60.5%) of a pale yellow solid containing three impurities; ^{31}P NMR (CH_2Cl_2) major signal at 67.7 and minor signals at 48.6 and 49.2 (sulfide **5**), 74.8 and 80.4. The two last signals could not be eliminated after another chromatography and two recrystallizations in CH_2Cl_2–EtOH; mp 262°C (decomp.).

Hydrogen-1 NMR ($CDCl_3$) δ2.0 (*s*, 12*H*, Me); 3.3 (*d*, $^2J_{HP}$ 11.7 Hz, 2*H*, PCH); 6.5 (*d*, $^3J_{HP}$ 39.0 Hz, 2*H*, =CH); 7.2–7.4 and 7.6–7.7 (*m*, 10*H*, Ph); minor signals at 1.66–1.94 (*m*), 3.7–4.5 (*m*) and 7.1 (*m*, at all ca. 2.5*H*). Carbon-13 NMR ($CDCl_3$) δ19.8 and 23.3 (*s*, CH_3); 57.0 (*d*, $^2J_{CP}$ 49.1 Hz); 126.8, 128.7, and 128.8 (*s*, aromatic CH); 127.3 (*s*, C_7 and C_{14}); 130.1 (*d*, J_{CP} 13.0 Hz), 133.4 (*s*) and 134.9 (*s*, C_4, C_5, C_{11}, C_{12}, and C-ipso). Mass spectrum (70 eV) *m/z* (relative intensity) 528 (M, 15), 496 (M–S, 65%), 463 (M–2S, 15), 232 [(M–2S)/2, 100)], 200[(M–4S)/2, 80)].

X-RAY STRUCTURE DETERMINATION FOR **5**

Crystals of **5**, $C_{26}H_{26}P_2S_3$, were obtained by slow diffusion of hexane into a toluene solution of the compound. Data were collected at 18 ± 1° on an Enraf Nonius CAD4 diffractometer. The crystal structure was solved and refined using the Enraf Nonius supplied SDP package. The compound crystallizes in space group *P*21/c, a = 16.008(2) Å, b = 11.042(1) Å, c = 15.963(1) Å, β = 115.41(1), V = 2548.56(1.3) Å^3; Z = 4; D_{calc} = 1.294 g · cm^{-3}; Mo K_α radiation (λ = 0.71073 Å) graphite monochromator; μ = 4.1 cm^{-1}; F(000) = 11040. A total of 4726 unique reflections were recorded in the range 2° ≤ 2θ ≤ 50°, of which 1764 were considered as unobserved [$F < 3\sigma(F)$], leaving 2963 for solution and refinement. The structure was solved by direct methods, yielding a solution for 15 of the 31 heavy atoms. The positional parameters of hydrogen atoms were refined in the final stages of least squares (B = 1.3 times the equivalent B of the attached carbon), while using anisotropic temperature factors for all other atoms. A non-Poisson weighting

scheme was applied with a p factor equal to 0.08. The final R factors were $R = 0.037$, $R_1 = 0.051$, GOF = 1.08.

SUPPLEMENTARY MATERIAL AVAILABLE

Expanded Tables of bond distances, bond angles, refined displacement parameter expressions (beta's), positional parameters, and 10* Fobs plus Fcalc. Ordering information is given on any masthead page.

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