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New Perthiophosphonic Acid Anhydrides and the Direct Indication of the Dimer-Monomer Equilibrium. NMR and X-Ray Studies

Haiko Beckmann, Gisbert Großmann,* and Gisela Ohms

Institut für Analytische Chemie der Technischen Universität Dresden, Mommsenstraße 13, 01062 Dresden, Germany

Joachim Sieler*

Institut für Anorganische Chemie der Universität Leipzig, Linnéstraße 3, 04103 Leipzig, Germany

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ABSTRACT

New perthiophosphonic acid anhydrides $(R\text{-}PS_2)_n$ *with R = 2,4,6-tri-iso-propylphenyl and 2,4-di-tert-butyl-6-methylphenyl have been prepared. For the latter case, the isolation of the monomer (n = 1), the 2,4-di-tert-butyl-6-methylphenyl-dithioxophosphorane, and both dimers (n = 2), cis- and trans-2,4-bis(2,4-di-tert-butyl-6-methylphenyl)-2,4-dithioxo-1,3,2,4-dithiadiphosphetane, of one perthiophosphonic acid anhydride has been performed for the first time. The crystal structure of 2,4-di-tert-butyl-6-methylphenyl-dithioxophosphorane and of cis-2,4-bis(2,4,6-tri-iso-propylphenyl)-2,4-dithioxo-1,3,2,4-dithiadiphosphetane has been determined. The new cis and trans dithiadiphosphetanes and dithioxophosphoranes as well as the known compounds* $(2,4,6\text{-trimethylphenyl-}PS_2)_2$ *and 2,4,6-tri-tert-butylphenyl-*PS_2 *are characterized by solution and high resolution solid-state* ^{31}P *and* ^{13}C *NMR spectroscopy. The existence of a dimer-monomer equilibrium is directly proved by 2D exchange* ^{31}P *NMR spectroscopy. It is shown that the reaction of the monomer with methanol is faster than the reaction of the dimer with methanol.*

INTRODUCTION

Dimeric perthiophosphonic acid anhydrides **1** (2,4-diorganyl-2, 4-dithioxo-1, 3, 2, 4-dithiadiphosphetanes), in particular the so-called LAWESSON reagent (R = *p*-methoxyphenyl), have been applied in many syntheses. According to Ref. [1], the introductory step of the investigated reactions consists of establishing the equilibrium between the dimeric **1** and the monomeric **2** (organyldithioxophosphorane) species followed by the reaction of the monomer with the reaction partners. This is supported by kinetic investigations of the reaction of **1** with benzophenone [2]. Other authors assume a direct attack of the reaction partner at the four-membered ring of the dimer [3].

Two isomeric forms of **1** can be detected in solutions of many perthiophosphonic acid anhydrides with various organic residues, e.g., **a** and **b**, by means of ^{31}P NMR spectroscopy, the dominant *trans* isomer, and the minor *cis* isomer [4]. A signal of the monomer organyldithioxophosphorane **2** has not been obtained in these solutions. On the other hand, with the sterically demanding substituent **c**, only the monomer **2c** occurs [5]. The formation of **2a** starting from **1a** has already been proved in gaseous phase by heating **1a** in vacuum [6].

From solutions of perthiophosphonic acid anhydrides with R = **a**, **b**, and others, only one isomer **1** was isolated by crystallization, in most cases the *trans* isomer being obtained [4b, 7–10]. Kinetic investigations into the *cis-trans* equilibrium of the dimer by Hahn et al. [11] suggest the existence of a tetramer.

In the present article, we describe the synthesis of perthiophosphonic acid anhydrides with the bulky substituents **d** and **e**. These substituents cause

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*To whom correspondence should be addressed.

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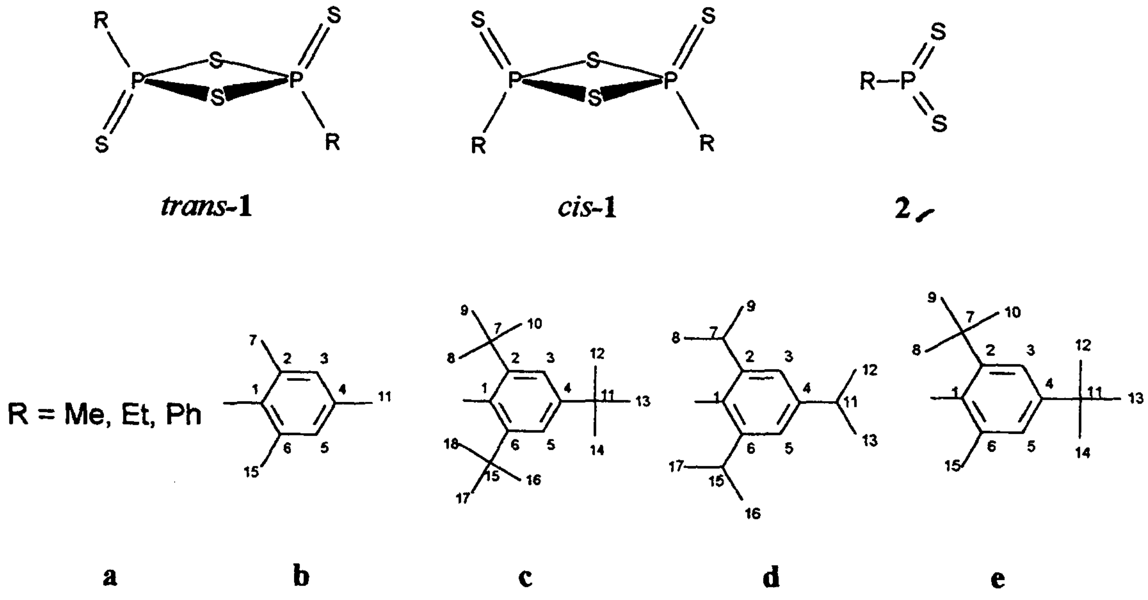


SCHEME 1

TABLE 1 Bond Lengths (Å) and Bond Angles (deg.) in the Molecular Structure of *cis*-2,4-bis(2,4,6-tri-*iso*-propylphenyl)-2,4-dithioxo-1,3,2,4-dithiadiphosphetane (*cis*-**1d**), 2,4-di-*tert*-butyl-6-methylphenyl-dithioxophosphorane (**2e**), and 2,4,6-tri-*tert*-butylphenyl-dithioxophosphorane (**2c**)[a]

	Distance				Angle		
Atoms	*cis*-**1d**	**2e**	**2c**[a]	*Atoms Row*	*cis*-**1d**	**2e**	**2c**[a]
P1–S1	2.118(2)	1.894(7)	1.890	S1–P1–S1′	90.09(5)	—	—
P1–S1′	2.139(1)	—	—	S1–P1–S2	115.75(6)	126.3(3)	126.0
P1–S2	1.916(1)	1.900(7)	1.891	S1′–P1–S2	118.00(6)	—	—
P1–C1	1.814(4)	1.808(5)	1.812	S1–P1–C1	105.9(1)	114.6(6)	117.9
C1–C2	1.421(6)	1.413(7)	1.426	S1′–P1–C1	109.2(1)	—	—
C2–C3	1.391(6)	1.404(8)	1.399	S2–P1–C1	115.0(1)	118.5(5)	116.1
C3–C4	1.363(7)	1.389(8)	1.378	P1–S1–P1′	88.81(5)	—	—
C4–C5	1.404(7)	1.391(8)	1.361	P1–C1–C2	120.5(3)	126.6(3)	119.5
C5–C6	1.407(6)	1.379(7)	1.390	P1–C1–C6	119.1(3)	111.9(3)	119.3
C6–C1	1.400(6)	1.414(7)	1.423	C1–C2–C3	118.0(3)	116.1(4)	116.3
C2–C7	1.498(6)	1.550(8)	1.549	C2–C3–C4	122.3(4)	123.5(5)	124.1
C7–C8	1.529(7)	1.52(3)	1.50	C3–C4–C5	119.2(4)	117.1(5)	117.1
C7–C9	1.551(6)	1.40(3)	1.53	C4–C5–C6	120.7(4)	123.0(4)	124.8
C7–C10	—	1.49(1)	1.50	C5–C6–C1	118.4(3)	118.1(4)	116.5
C4–C11	1.537(7)	1.537(7)	1.527	C6–C1–C2	120.3(3)	121.5(4)	121.3
C11–C12	1.473(8)	1.44(4)	1.52	C1–C2–C7	123.7(3)	126.1(4)	127.8
C11–C13	1.46(1)	1.53(2)	1.52	C3–C2–C7	118.1(4)	117.3(4)	115.9
C11–C14	—	1.51(1)	1.51	C3–C4–C11	119.4(4)	122.6(4)	122.7
C6–C15	1.521(6)	1.516(9)	1.547	C5–C4–C11	121.2(4)	120.3(4)	120.2
C15–C16	1.547(6)	—	1.51	C5–C6–C15	118.4(3)	118.6(5)	115.6
C15–C17	1.524(6)	—	1.52	C1–C6–C15	123.0(3)	123.2(4)	127.9
C15–C18	—	—	1.50				
C1s–C2s[b]	1.43(1)	—	—				
C2s–N1s[b]	1.17(2)	—	—				

[a] Data from Ref. [5a].

[b] Acetonitrile as a solvate in the crystal.

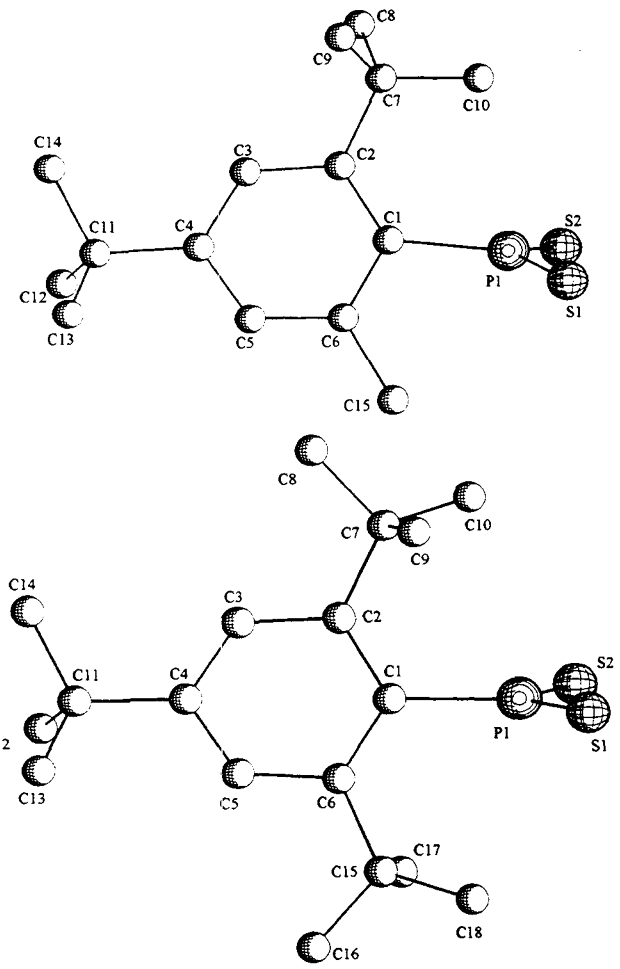


FIGURE 1 Molecular structure of organyl-dithioxophosphoranes. Above: 2,4-di-*tert*-butyl-6-methylphenyl-dithioxophosphorane (**2e**). Below: 2,4,6-tri-*tert*-butylphenyl-dithioxophosphorane (**2c**) (according to Ref. [5]).

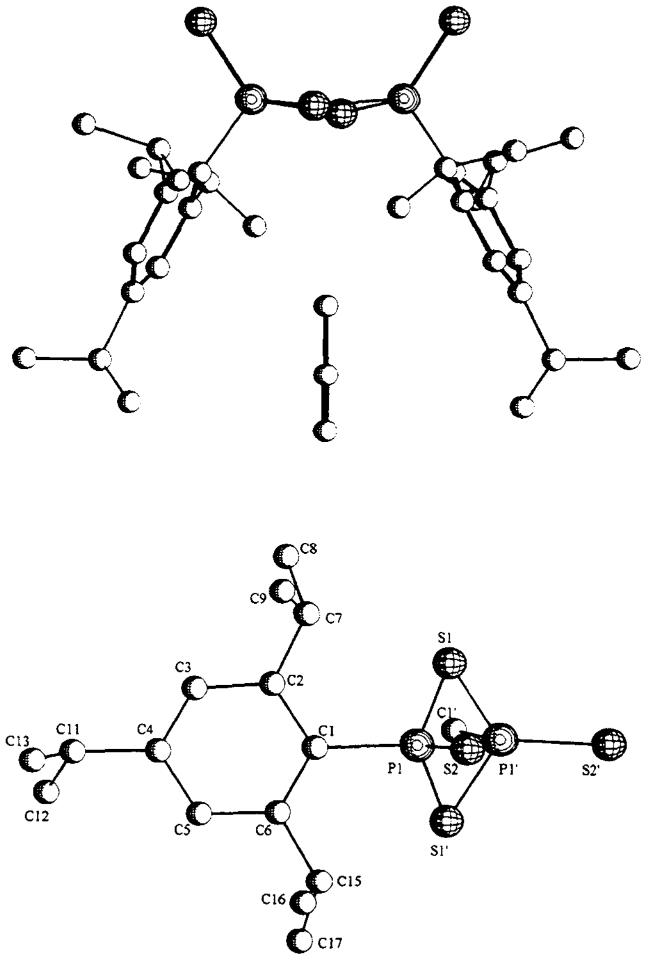


FIGURE 2 Molecular structure of *cis*-2,4-bis(2,4,6-tri-*iso*-propylphenyl)-2,4-dithioxo-1,3,2,4-dithiadiphosphetane (*cis*-**1d**). Above: Complete molecule. Below: Presentation without the second phenyl ring for better comparison with the organyl-dithioxophosphoranes of Figure 1.

a steric hindrance smaller than that of **c** and greater than that of **b**. Such perthiophosphonic acid anhydrides should allow the direct observation of the dimer-monomer equilibrium. Furthermore, perthiophosphonic acid anhydrides with the substituents **b** and **c** have been synthesized in order to compare their NMR data with the values of the new compounds.

RESULTS AND DISCUSSION

The perthiophosphonic acid anhydrides **d** and **e** have been prepared by reaction of the corresponding phosphanes RPH_2 with elemental sulfur according to Ref. [12]. The reaction of RPH_2 (R = **d**) with sulfur in toluene leads to a crude product from which *cis*-**1d** and *trans*-**1d** can be isolated by treatment with acetonitrile and toluene, respectively. Compound **2d** is detectable only in solution. The two dimers can be separated because of the sufficiently slow isomerization at ambient temperature.

We have carried out the reaction of RPH_2 (R = **e**) with sulfur as described previously in an article by Ionkin et al. [13] but already before their paper was published. Similar to their observations, a highly viscous crude product was obtained which crystallized after about 2 weeks. While Ionkin et al. described only the existence of the monomer **2e** as the main component of the crude product, we have been able to isolate **2e** and small amounts of both dimers *cis*-**1e** and *trans*-**1e**. **2e** has been purified by recrystallization from acetonitrile. The monomer and the *cis* dimer crystallize at the same time and can be separated mechanically. The iso-

TABLE 2 Selected Torsion Angles in the Molecular Structure of *cis*-2,4-bis(2,4,6-tri-*iso*-propylphenyl)-2,4-dithioxo-1,3,2,4-dithiadiphosphetane (*cis*-**1d**), 2,4-di-*tert*-butyl-6-methylphenyl-dithioxophosphorane (**2e**), and 2,4,6-tri-*tert*-butylphenyl-dithioxophosphorane (**2c**)

Number	*Atoms Row*	*cis*-**1d**	**2e**	**2c**[a]	*Atoms Row*	*cis*-**1d**	**2e**	**2c**[a]
1	C1–C2–C3–C4	2.6	10.0	−0.1	C2–C3–C4–C5	5.3	−6.8	0.2
2	C3–C4–C5–C6	−4.9	1.1	0.6	C4–C5–C6–C1	−3.4	0.8	−1.5
3	C5–C6–C1–C2	11.4	2.7	1.5	C6–C1–C2–C3	−11.1	−7.8	−0.8
4	C15–C6–C5–C4	171.8	178.2	179.0	C7–C2–C3–C4	−172.4	−177.2	−179.8
5	C15–C6–C1–P1	13.6	4.3	2.4	C7–C2–C1–P1	−13.4	1.5	−2.5
6	C15–C6–C1–C2	−163.5	−174.5	−179.0	C7–C2–C1–C6	163.7	−179.8	178.9
7	S1–P1–C1–C2	−40.9	91.4	81.4	S1–P1–C1–C6	46.2	−87.4	100.0
8	S1′–P1–C1–C2	−136.7	—	—	S1′–P1–C1–C6	142.0	—	—
9	S2–P1–C1–C2	91.1	−97.6	98.7	S2–P1–C1–C6	−86.0	83.6	80.0
10	C11–C4–C3–C2	−178.3	172.6	−178.8	C11–C4–C5–C6	178.7	−178.4	179.7
11	P1–C1–C2–C3	171.9	173.5	177.8	P1–C1–C6–C5	−171.5	−178.4	−177.1
12	C8–C7–C2–C3	−57.9	−64.4	−16.4	C16–C15–C6–C5	−71.4	—	−28.2
13	C9–C7–C2–C3	65.9	50.5	99.8	C17–C15–C6–C5	52.8	—	93.3
14	C10–C7–C2–C3	—	169.5	−139.2	C18–C15–C6–C5	—	—	−144.5
15	C12–C11–C4–C3	127.5	118.6	122.5	C12–C11–C4–C5	−56.2	−62.0	−56.5
16	C13–C11–C4–C3	−94.6	−121.6	−119.8	C13–C11–C4–C5	81.8	57.8	61.2
17	C14–C11–C4–C3	—	2.5	0.7	C14–C11–C4–C5	—	−178.1	−178.3

[a] Data from Ref. [5a].

TABLE 3 ^{31}P NMR Data of Dithiadiphosphetanes and Dithioxophosphoranes in Solution and in the Solid State (Chemical Shifts in ppm, $^{2}J_{PP}$ in Hz)

Compound	*Solution in CDCl$_3$*		δ_{iso}			
	δ	$^{2}J_{PP}$	δ_{11}	δ_{22}	δ_{33}	
trans-**1b**	25.9[a]	6.8	24.6	203	94	−224
cis-**1b**	24.0[b]	7.0[b]	—	—	—	—
trans-**1d**	29.2	7.0	28.1	213	97	−226
cis-**1d**	31.4	3.4	28.5	232	91	−238
trans-**1e**	34.6[c]	9.1	33.2	225	92	−218
cis-**1e**	29.0[c]	10.6	27.3/28.0	217	98	−232
2b	279.1[d]	—	—	—	—	—
2c	295.1		301.0	601	197	105
2d	284.6[e]		—	—	—	—
2e	289.4		294.0	590	182	111

[a] In Ref. [8b], a value of 11.47 ppm is given for a solution in toluene.

[b] Determined from mixture with *trans*-**1b**.

[c] At low temperature, two rotamers become visible (see Ref. [22]).

[d] At 393 K, in *ortho*-dichlorobenzene, in a mixture with *cis*-/*trans*-**1b**.

[e] From mixture with *cis*-/*trans*-**1d** after heating of 373 K for 5 minutes in a sealed tube.

lation of both *cis* and *trans* dimers as well as the monomer of *one* perthiophosphonic acid anhydride has been performed for the first time.

In the reaction of RPH_2 (R = **b**) with sulfur, two isomers **1** were formed but only *trans*-**1b** crystallized from solution.

Molecular and Crystal Structures

The molecular structure and the atomic labeling of the compounds **2e** and *cis*-**1d** are shown in Figures 1 and 2. Bond distances and bond angles are given in Table 1, and selected torsion angles are shown in Table 2.

The different size of the two *ortho*-substituents in **2e** leads to rather different bond angles P1-C1-C2 (126.6°) and P1-C1-C6 (111.9°) compared to the two alike angles (119.5° and 119.3°) in **2c**. The flatness of the phenyl ring of **2e** is significantly disturbed (lines 1–3 of Table 2). The PS_2 unit is twisted by about 80–90° in **2c** and **2e** with respect to the phenyl ring (compare lines 7 and 9 of Table 2). In ylide-substituted dithioxophosphoranes described by Jochem et al. [14], the sulfur atoms are situated in the plane given by C_1 and the attached atoms. As some of the C–C bond lengths of the *tert*-butyl groups of **2e** are shortened, a strong thermal mo-

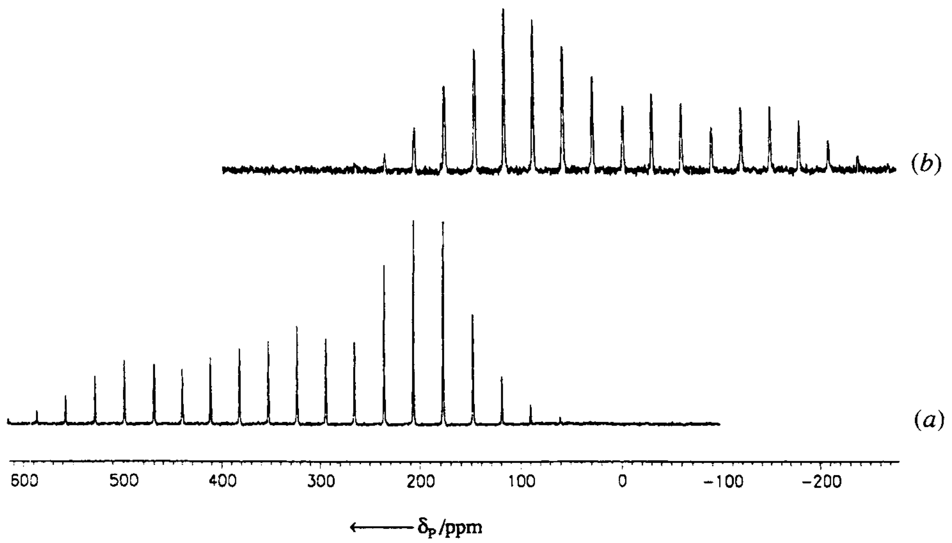


FIGURE 3 ^{31}P CP MAS spectra of (a) 2,4-di-*tert*-butyl-6-methylphenyl-dithioxophosphorane (**2e**) and (b) *trans*-2,4-bis(2,4,6-tri-*iso*-propylphenyl)-2,4-dithioxo-1,3,2,4-dithiadiphosphetane (*trans*-**1d**). Spinning frequencies: (a) 3.55 kHz and (b) 3.60 kHz.

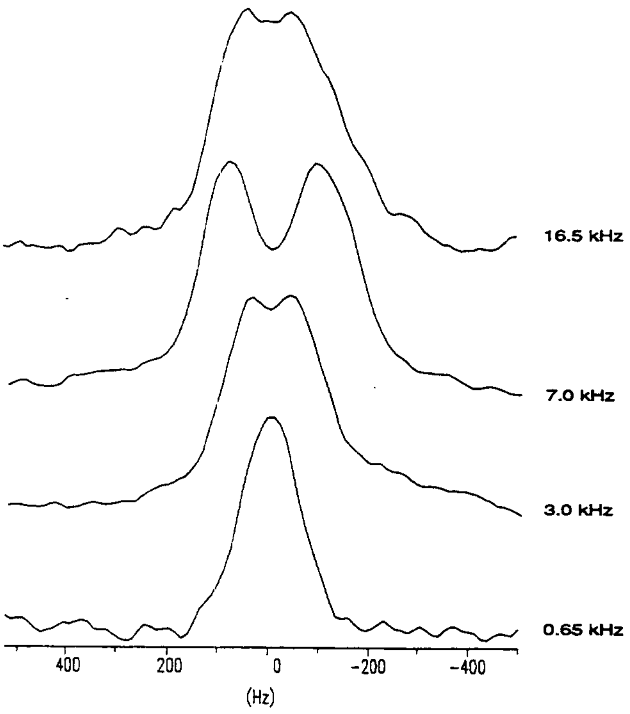


FIGURE 4 ^{31}P CP MAS spectra of *cis*-2,4-bis(2,4,6-tri-*iso*-propylphenyl)-2,4-dithioxo-1,3,2,4-dithiadiphosphetane (*cis*-**1d**) at different spinning frequencies. Only the isotropic line is shown.

bility of these groups may be deduced. A torsion of the *tert*-butyl groups around the bond to the phenyl ring is possible in the crystalline state where the methyl groups are situated in equivalent positions.

In the lattice of *cis*-**1d**, one molecule of acetonitrile per dithiadiphosphetane molecule is included. The dithiadiphosphetane ring of *cis*-**1d** is bent with a dihedral angle of 16.0° between the S1-P1-S1′ and S1-P1′-S1′ planes. Obviously, the two organic residues require more space than the S2 atoms. A similar situation has been described for *cis*-diazadiphosphetidines [15]. Up to now, there is only one crystal structure known of a *cis*-dithiadiphosphetane. In this case, in which the *cis*-dithiadiphosphetane is bridged over a 1,8-disubstituted naphthalene [16], the $(PS)_2$ ring is bent by 15° in the opposite direction.

In *cis*-**1d** the endocyclic P–S bond lengths are slightly different. This provides evidence for a sufficiently easy cleavage of the dimer compound leading to two monomer units. A difference of the endocyclic bond lengths of *trans*-dithiadiphosphetanes with R = Ph and R = mesityl has been already observed by Lensch and Sheldrick [8b].

While in *trans*-dithiadiphosphetanes with R = *p*-methoxyphenyl [10] and R = Ph [8a] the phenyl rings are located in or nearly in the S2-P1-C1 plane, they are almost perpendicular to this plane in the compound with R = mesityl [8b] and also in *cis*-**1d**. This orientation is attributed to the substituents in the *ortho*-position.

For the *ortho*-*iso*-propyl residues, some C–C bond distances are found to be very short. Therefore, a thermal mobility of these groups can be as-

TABLE 4 ^{13}C NMR Data of Dithiadiphosphetanes and Dithioxophosphoranes in the Solid State and in Solution of CDCl$_3$ (Chemical Shifts in ppm, P–C coupling constants in Hz)

						$\delta_{(solid)}$ $\delta_{(solution)}$ $^nJ_{PC}(n)$						
Composition	*C1*	*C2*	*C6*	*C3*	*C5*	*C4*	*C7*	*C8/C9/C10*	*C11*	*C12/C13/C14*	*C15*	*C16/C17/C18*
trans-**1b**^{a}	138.9	139.7^b	138.4^b	130.7		143.3	24.5	—	22.6	—	23.4	—
	137.72	137.65		130.63		141.93	22.72		21.09		22.72	
	89.8(1)/1.5(3)	13.4(2)/−0.6(4)		14.4(3)/0.0(5)		3.3(4 + 6)	8.9(3 + 5)		—		8.9(3 + 5)	
cis-**1b**^{a}	—	—		—		—	—	—	—	—	—	—
	137.11	137.77		130.41		141.66	22.45		20.97		22.45	
	93.3(1 + 3)	12.6(2 + 4)		14.6(3 + 5)		3.3(4 + 6)	8.9(3 + 5)		—		8.9(3 + 5)	
trans-**1d**	139.0	149.0^b	148.6^b	125.4^b	122.0^b	153.7	35.3	−/(26.7/26.7)^c	36.6	24.1/24.1/− 23.7	35.3	−/(26.7/25.8)^c
	137.0	148.8		123.0		152.9	33.9	24.4	34.3		33.9	24.4
	92.3(1)/0.5(3)	14.0(2)/−0.6(4)		13.5(3)/0.7(5)		3.0(4 + 6)	10.2(3 + 5)	—	—	—	10.2(3 + 5)	—
cis-**1d**^{d}	138.1	152.8^b	149.8^b	123.7		154.6	35.5^b	−/(27.6/22.8)^c	36.5^b	29.0/22.8/− 23.5	34.9^b	−/(26.9/23.6)^c
	135.7	149.0		122.9		152.8	33.9	24.3	34.1		33.9	24.3
	94.6(1)/0.1(3)	13.8(2)/0.4(4)		13.8(3)/0.8(5)		3.1(4 + 6)	10.4(3 + 5)	—	—	—	10.4(3 + 5)	—
trans-**1e**	140.1	149.0	140.1	125.3	128.7	155.1	39.4	35.8^e	35.8	31.5^e	23.0	—
	138.5	151.0	139.4	124.8	126.8	153.4	38.9	34.6	34.7	30.9	23.1	
	82.0(1)/1.0(3)	10.8(2)/−0.4(4)	14.1(2)/−0.7(4)	15.5(3)/−0.3(5)	13.9(3)/−0.5(5)	3.6(4 + 6)	—	—	—	—	11.6(3 + 5)	
cis-**1e**^{f}	140.0	149.5/152.8	140.0/142.8	124.6/126.0	126.6/127.6	154.6	39.9 + 38.5	32.6^e + 36.2^e	36.2 + 35.0	31.0^e	21.4 + 27.3	—
	138.5	150.9	139.8	124.0	126.6	152.8	38.7	34.2	34.5	30.9	23.0	
	≈87(1 + 3)	10.6(2)/−0.2(4)	14.5(2)/−1.1(4)	14.5(3)/0.1(5)	13.9(3)/−0.5(5)	3.6(4 + 6)	—	—	—	—	11.6(3 + 5)	
2c	141.5	149.5		123.8	125.6	154.0	39.0	35.5^e	36.6	32.3^e	39.0	34.0^e
	141.4	149.6		124.0		153.5	38.9	34.3	35.3	31.0	38.9	34.3
	59.8(1)	10.4(2)		14.6(3)		3.5(4)	2.5(3)	—	—	—	2.5(3)	—
2e	142.8	149.8	135.2	124.2	127.9	155.2	38.4	33.8^e	36.2	32.8^e	23.9	—
	142.9	148.6	135.3	122.7	126.1	153.5	37.7	33.5	35.0	31.0	23.6	
	69.6(1)	10.0(2)	10.4(2)	14.0(3)	12.8(3)	3.1(4)	2.4(3)	—	—	—	8.5(3)	

[a] $\delta_{(solution)}$ and $^nJ_{PC}(n)$ from a mixture of *cis-/trans*-**1b**.

[b,c] May be exchanged.

[d] The crystals contain acetonitrile, δ_C = −2.4 (CH$_3$), and 118 (CN) ppm.

[e] For three methyl groups, one signal was obtained owing to rotational motion.

[f] Two groups of signals were obtained for the two organic rests.

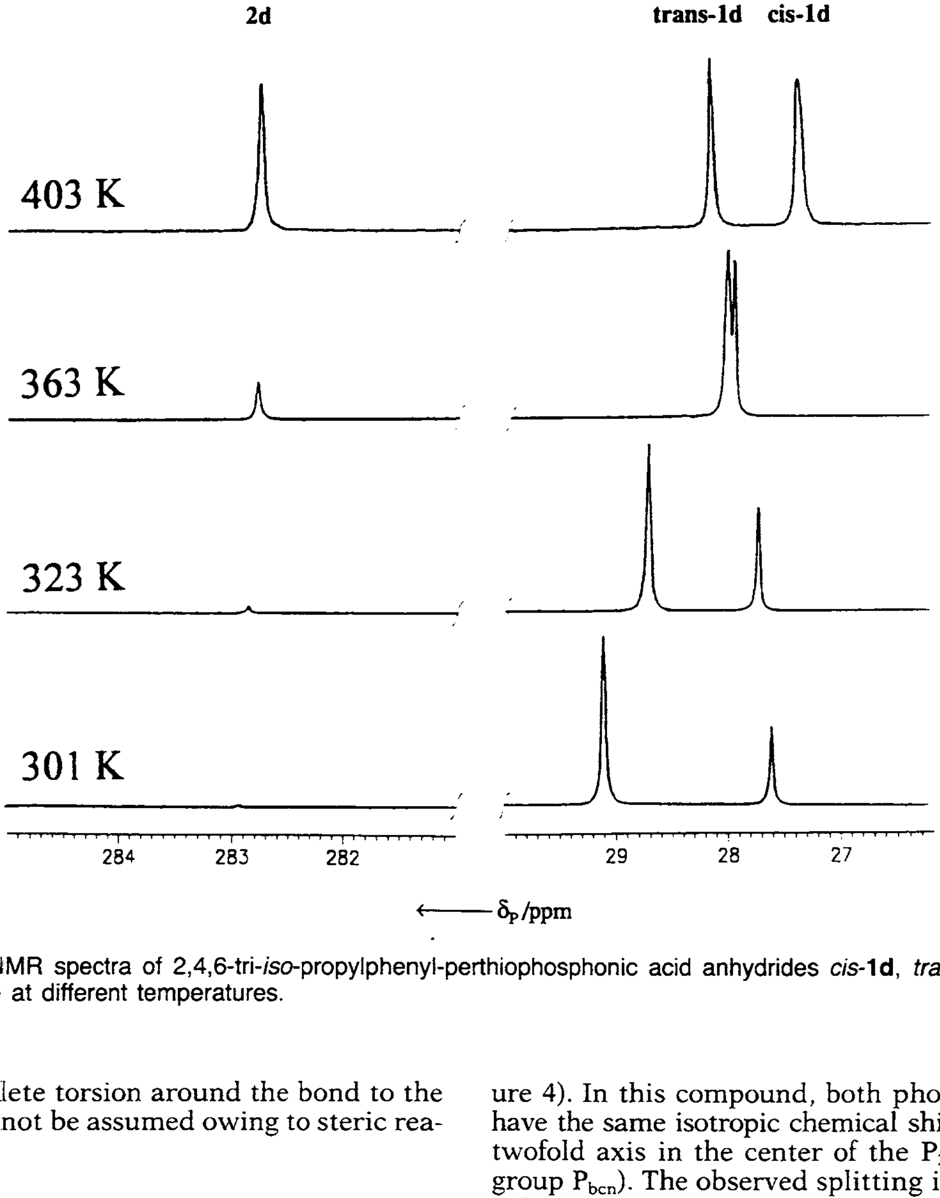


FIGURE 5 ^{31}P NMR spectra of 2,4,6-tri-*iso*-propylphenyl-perthiophosphonic acid anhydrides *cis*-**1d**, *trans*-**1d**, and **2d** in *o*-dichlorobenzene at different temperatures.

sumed. A complete torsion around the bond to the phenyl ring cannot be assumed owing to steric reasons.

NMR in Solution and the Solid State

NMR spectra in solution and the solid state were used for the structure elucidation of the different compounds. The ^{31}P NMR data are compiled in Table 3. The monomer is easy to recognize because of its extremely lowfield ^{31}P chemical shift (about δ290). The chemical shift of the dimer four-membered ring is much smaller, between δ 65 and −5. *Cis*- and *trans*-isomers of **1** cannot be distinguished by the ^{31}P chemical shift in solution only. Although in most cases the chemical shift of the *cis*-isomer is smaller, this reverses for **1d**.

A comparison of the ^{31}P CP MAS spectra of *trans*-**1d** and **2e** (Figure 3) shows clearly the large difference of the chemical shift tensors of dimer and monomer perthiophosphonic acid anhydrides. The MAS spectrum of *cis*-**1d** is characterized by a spinning frequency-dependent sideband splitting (Figure 4). In this compound, both phosphorus atoms have the same isotropic chemical shift owing to the twofold axis in the center of the P_2S_2 ring (space group P_{bcn}). The observed splitting is caused by dipolar interaction of the two P atoms and different orientations of their chemical shift tensors [17]. ^{31}P CP MAS spectra of *trans*-**1b**, **d**, and **e** do not show such a splitting.

The principal values of the ^{31}P chemical shift tensor obtained from the spectra of the investigated dithiadiphosphetanes differ only slightly due to steric similarity of the substituents R. Significant differences occur in the principal values δ_{22} compared to the corresponding values for R = Ph (δ 130) and R = *p*-methoxyphenyl [18] (δ 141), whereas δ_{11} and δ_{33} are quite similar to those of the compounds of comparison. As the results of MAS experiments do not give any information concerning the orientation of the principal axes with respect to the molecular frame, IGLO calculations of the shielding tensor [19] of a model molecule with R = Me are taken into consideration. According to these calculations, the principal axis 2 is perpen-

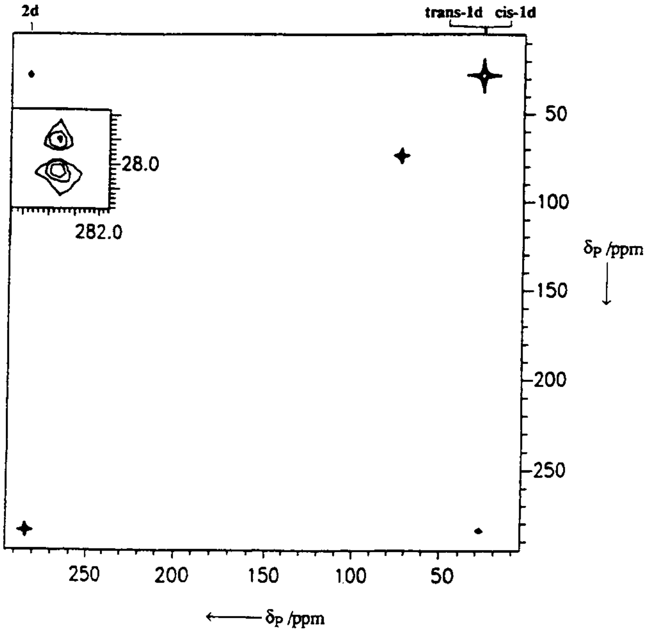


FIGURE 6 ^{31}P 2D exchange NMR spectrum of 2,4,6-tri-*iso*-propylphenyl-perthiophosphonic acid anhydrides *cis*-**1d**, *trans*-**1d**, and **2d** in *o*-dichlorobenzene 393 K. NOESY pulse sequence, τ_m = 100 ms, SI2 = 4K, SI1 = 2K spectrum, 17 Hz/Pt, 12 hours. The final matrix was symmetrized prior to plotting.

dicular to the C–P=S plane. Although in the compounds investigated this plane is not strictly a mirror plane (the phenyl group is not exactly perpendicular with respect to the C–P=S plane), we expect a similar orientation of axis 2.

Deshielding contributions to a principal value are mainly caused by atoms situated in a plane including the nucleus investigated and being perpendicular to a principal axis. Therefore, principal values δ_{22} are about 30–40 ppm smaller in the case of the compounds investigated here with phenyl groups turned out of the C–P=S plane and *o*-substituents situated in the γ-position with respect to the P atom.

Both the dithioxophosphoranes **2c** and **2e** show similar principal values of the ^{31}P chemical shift tensor. According to IGLO calculations for a model compound with R = Ph [19], the principal axis 1 intersects the angle S=P=S, the principal axis 2 is situated in the S=P=S plane, and the principal axis 3 is perpendicular with respect to this plane. The very high principal value δ_{11} is caused by the strong deshielding effect of the π-bonds in the S=P=S system.

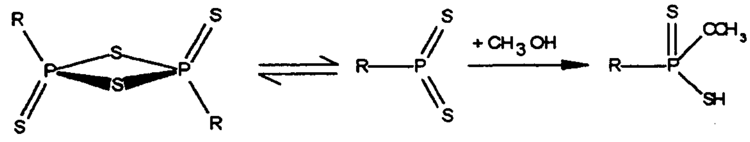
The assignment of the ^{13}C signals in the solution spectra causes no difficulties (see Table 4). The ^{31}P–^{13}C coupling patterns occurring are typical for an ABX spin system with very small differences ν_B-ν_A; hence, it originates from a symmetric compound containing two P atoms, the dimer. The vicinal *cis* coupling constant $^3J_{PC}$ of the quaternary C atoms of the *ortho-tert*-butyl groups of 2.5 Hz is surprisingly low compared to ca. 9 Hz in the case of the values for the *ortho*-methyl groups.

The ^{13}C CP-MAS spectra are in agreement with the known crystal structures. In the case of *trans*-**1b**, different signals are observed for C2 and C6 and both *ortho*-methyl groups, as the phenyl rings are not precisely perpendicular with respect to the C–P=S plane. Spectra of *cis*-**1d** show additional different signals of C3 and C5 and two methyl groups of one *iso*-propyl group. The high chemical shift in the range of the methyl groups is assigned to C12 due to a deshielding effect of the anisotropy cone of the included acetonitrile. As only three methyl signals of the same intensity are observed for nine groups in *trans*-**1e**, a sufficiently fast rotation of the *tert*-butyl groups around the bond to the phenyl ring must occur in the solid state. The same is valid for *cis*-**1e**, **2c**, and **2e**. From the twofold number of ^{13}C signals of *cis*-**1e**, the conclusion may be drawn that the molecule has C_1-symmetry.

For the study of the dimer-monomer exchange, the compounds *cis*- and *trans*-**1d** were used, as these are still present in dimeric form. After dissolving *cis*-**1d** in *ortho*-dichlorobenzene, *trans*-**1d** can be observed after several hours while **2d** is detected only in traces. By heating this solution, an equilibrium between *cis*-**1d** and *trans*-**1d** is established and the concentration of **2d** increases considerably (see Figure 5). At 393 K, all three compounds have comparable concentrations.

A ^{31}P 2D exchange NMR spectrum (see Figure 6) at this temperature proves the exchange of both dimers **1d** with the monomer **2d**.

After the solution has been cooled to ambient temperature, the portion of *cis*-**1d** is much greater than that of *trans*-**1d** (about 2:1). This can only be explained by the influence of the polar solvent and the arrangement of the substituents, where the phenyl ring is perpendicular to the S=P–C plane.



SCHEME 2

TABLE 5 Summary of Crystal Data, Data Collection, and Structure Refinement

Formula	*Compound* **1d** *$(C_{15}H_{23}PS_2)_2 \cdot CH_3CN$*	*Compound* **2e** *$C_{15}H_{23}PS_2$*
Color, habit	colorless, prisms	yellow, needles
Crystal size (mm)	0.24 × 0.25 × 0.30	0.15 × 0.22 × 0.32
Crystal system	orthorhombic	orthorhombic
Space group	Pbcn	$Pna2_1$
Unit cell dimensions (Å)	a = 17.878(2) b = 15.134(2) c = 13.337(1)	a = 15.277(2) b = 11.364(2) c = 9.659(1)
Volume (Å^3)	3608.5	1676.9
Z	4	4
Formula weight	553.6	262.3
Density (calc.)	1.02 g cm^{-3}	1.04 g cm^{-3}
Absorption coefficient	2.74 cm^{-1}	2.78 cm^{-1}
Diffractometer	STADI4 (Fa STOE)	
Radiation	Mo $K_\alpha(\lambda = 0.71069$ Å)	
Scan type	$\omega/2\theta$	
2 Theta range	3–50	3–55
Index range	h = 0–14 k = 0–17 l = 0–21	h = 0–17 k = 0–14 l = 0–12
Reflection collected	4297	2287
Independent reflections	2813	1719
Observed reflections F(hkl) > 3σF(hkl)	2075	1501
Number of parameters refined	202	173
Final R indices	R = 0.056 R_w = 0.054	R = 0.057 R_w = 0.062
Weighting scheme	$w = 1/\sigma^2(F) + 0.00109F^2$	$w = 1/\sigma^2(F) + 0.0037F^2$
Largest difference peak	0.4	0.5
Largest difference hole	0.2	0.3
Program used	SHELX76, SHELXS86	

Thus, an energetically favored position of the phenyl rings (quasiparallel) is achieved in the *cis*-isomer (see Figure 2). Otherwise, the phenyl ring in the LAWESSON reagent [10] is situated exactly in this S=P–C plane. Consequently, no *cis*-isomer can be detected in the case of this compound [4a].

The existence of the dimer-monomer equilibrium between the compounds *cis-/trans-***1e** and **2e** cannot be proved, as the dimers undergo irreversible transformation into the monomer when the solutions are heated.

In the following paragraphs, the different reactivities of monomer and dimer are discussed. *Cis-***1d** is first dissolved in hot *ortho*-dichlorobenzene. Fast cooling of this solution freezes the equilibrium composition. The resulting yellow solution contains both dimers and the monomer in a remarkable concentration. When methanol is added, the solution loses its color immediately and the signal of the monomer disappears from the ^{31}P NMR spectrum. Instead, the signal of the corresponding dithiophosphonic acid O-methyl ester (δ_P = 91.0), the product of the methanolysis reaction, is observed. Despite the presence of an excess of methanol, the dimers can be detected for several hours.

Our experimental results give evidence for the mechanism of the reaction between dimeric perthiophosphonic acid anhydrides with nucleophiles discussed in the literature, which has been only an assumption up to now. In the first step of the reaction, the dimer forms two monomers, which then react with the nucleophile.

The reaction of aliphatic perthiophosphonic acid anhydrides $(RPS_2)_2$ should proceed in the same manner. When *trans*-(*cy*-Hex-$PS_2)_2$ is dissolved in 1,2-dichloroethane, about one-third is converted into the corresponding *cis*-isomer. If the same experiment is carried out using 1,2-dichloroethane containing 5 vol % methanol, no *cis*-isomer can be detected. Besides the signal of the *trans*-isomer, only that of the methanolysis product is observed (*cy*-HexP(S)(OH)(OCH_3) at δ_P = 110.7). Thus, the monomer *cy*-HexPS_2 occurring in the equilibrium reacts immediately with methanol without forming the *cis*-isomer.

EXPERIMENTAL

The NMR spectra were run on a Bruker MSL 300 (121.495 MHz for ^{31}P and 75.475 MHz for ^{13}C). For

TABLE 6 Atomic Parameters with Standard Deviations in Parentheses for Compound *cis*-**1d**

Atom	*x/a*	*y/b*	*z/c*
P1	0.4371(1)	0.6108(1)	0.1767(1)
S1	0.5559(1)	0.6246(1)	0.1655(1)
S2	0.3929(1)	0.5032(1)	0.1296(1)
C1	0.3980(2)	0.7110(2)	0.1234(3)
C2	0.3375(2)	0.7548(2)	0.1715(3)
C3	0.3161(2)	0.8369(2)	0.1349(4)
C4	0.3494(3)	0.8744(3)	0.0527(4)
C5	0.4025(2)	0.8260(2)	−0.0010(3)
C6	0.4261(2)	0.7424(2)	0.0321(3)
C7	0.2913(2)	0.7143(3)	0.2532(3)
C8	0.2854(3)	0.7719(3)	0.3469(3)
C9	0.2128(2)	0.6930(4)	0.2108(4)
C11	0.3243(3)	0.9668(3)	0.0187(5)
C12	0.3872(3)	1.0289(3)	0.0069(7)
C13	0.2671(4)	0.9652(4)	−0.0602(5)
C15	0.4755(2)	0.6872(2)	−0.0364(3)
C16	0.5452(2)	0.7348(3)	−0.0739(4)
C17	0.4279(3)	0.6537(3)	−0.1250(3)
C1L	0.5000(1)	−0.1067(5)	0.2500(1)
C2L	0.5000(1)	−0.0119(6)	0.2500(1)
N3L	0.5000(1)	0.0650(6)	0.2500(1)

temperature-controlled measurements, a B-VT 1000 unit was used. For the determination of the anisotropy parameter, ^{31}P CP MAS spectra were measured at spinning frequencies of 2.5–4.0 kHz using cross polarization with a pulse sequence containing two contact pulses [20]. The spinning sideband systems have been computed by means of the program MASNMR of Jeschke [21]. The uncertainties of the principal values of the chemical shift tensors are ±5 ppm. The principal elements have been labeled according to the convention $\delta_{11} \geq \delta_{22} \geq \delta_{33}$.

TABLE 7 Atomic Parameters with Standard Deviations in Parentheses for Compound **2e**

Atom	*x/a*	*y/b*	*z/c*
P1	0.3614(1)	0.2001(1)	0.5572(1)
S1	0.3433(5)	0.2680(5)	0.3804(8)
S2	0.3369(3)	0.2717(4)	0.7306(9)
C1	0.3889(4)	0.0454(4)	0.5568(22)
C2	0.4735(4)	−0.0036(5)	0.5505(21)
C3	0.4787(4)	−0.1266(5)	0.5637(23)
C4	0.4060(4)	−0.2003(5)	0.5591(22)
C5	0.3242(4)	−0.1469(5)	0.5568(22)
C6	0.3129(4)	−0.0266(5)	0.5537(27)
C7	0.5611(4)	0.0655(5)	0.5525(23)
C8	0.6051(17)	0.0487(27)	0.6890(19)
C9	0.6195(14)	0.0186(22)	0.4551(26)
C10	0.5529(7)	0.1923(10)	0.5114(28)
C11	0.4140(4)	−0.3351(5)	0.5568(23)
C12	0.3706(22)	−0.3807(14)	0.6790(34)
C13	0.3693(8)	−0.3828(11)	0.4259(14)
C14	0.5077(7)	−0.3774(7)	0.5662(35)
C15	0.2209(5)	0.0225(6)	0.5494(34)

Crystal and intensity data are summarized in Table 5. Cell dimensions were determined by a least-squares refinement of the 20 values of 80 reflections. The final coordinates are compiled in Table 6 (*cis*-**1d**) and Table 7 (**2e**).

Further details of the crystal structure determination can be obtained from Fachinformationszentrum Energie, Physik, Mathematik GmbH, D-76344 Eggenstein-Leopoldshafen 2, Germany, on quoting the depository number CDS-400490 for compound **1d** and CDS 400481 for compound **2e**.

Reaction of 2,4,6-Trimethylphosphane with Sulfur. 18.4 g RPH_2 R = **b** in 100 mL toluene was added slowly to a suspension of 11.6 g sulfur in 200 mL toluene and then refluxed for 2 hours. Oxygen and moisture must be excluded. After cooling the solution, *trans*-**1b** crystallized forming fine colorless needles. Yield 20.8 g (81%).

Reaction of 2,4,6-Tri-iso-propylphenylphosphane with Sulfur. To a suspension of 6.18 g sulfur in 200 mL toluene 15.0 g RPH_2 with R = **d** in 100 mL toluene was added slowly, and then the mixture was refluxed for 2 hours. Oxygen and moisture must be excluded carefully. The solution was cooled, and the solvent was removed under vacuum. To the residue 150 mL acetonitrile was added. The microcrystalline white precipitate was separated by filtration, washed with acetonitrile, and dried under vacuum for 2 hours (13.0 g crude product). From the clear acetonitrile solution, pure *cis*-**1d** (1.2 g) crystallized overnight. Pure *trans*-**1d** was obtained after repeated washing of the crude product with toluene.

Reaction of 2,4-Di-tert-butyl-6-methylphenylphosphane with Sulfur. Under exclusion of oxygen and moisture, 19.0 g RPH_2 with R = **e** in 100 mL toluene was dropped into a suspension of 7.73 g sulfur in 200 mL toluene, and then the mixture was refluxed for 2 hours. After cooling, the solvent was removed under vacuum. A red-brown highly viscous product was obtained which crystallized after 14 days. The solid product was crushed and washed with a small amount of acetonitrile. The clear acetonitrile solution was concentrated under vacuum to about half its volume until it became turbid. *Cis*-**1e** formed small colorless crystals and **2e** yellow to orange crystals during precipitation overnight, which were separated mechanically. The remaining solid product was washed several times with small amounts of acetonitrile until only small colorless crystals of *trans*-**1e** remained.

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