

# Synthesis and Crystal Structure of the First "1,2-Diphospha[4]radialene"

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1,2-Diphosphetane **4**, the first "1,2-diphospha[4]radialene", has been prepared in 83% yield by the reductive coupling reaction of 2,3-bis(chloroisopropylphosphanyl)butadiene **3a** with lith-

ium in THF. The X-ray crystal structure of **4** was determined, and it shows that **4** is a highly strained 1,2-diphosphetane.

Carbon-phosphorus heterocycles possessing an endocyclic P–P bond have gained a continual interest in the last decades<sup>[1]</sup>. 1,2-Diphosphetanes are accessible by [2 + 2] cycloaddition, on the one hand by head-to-head dimerization of suitably substituted phosphalkenes<sup>[2]</sup> and on the other hand by reaction of a transition-metal-substituted diphosphene with electron-deficient alkenes<sup>[3]</sup>.

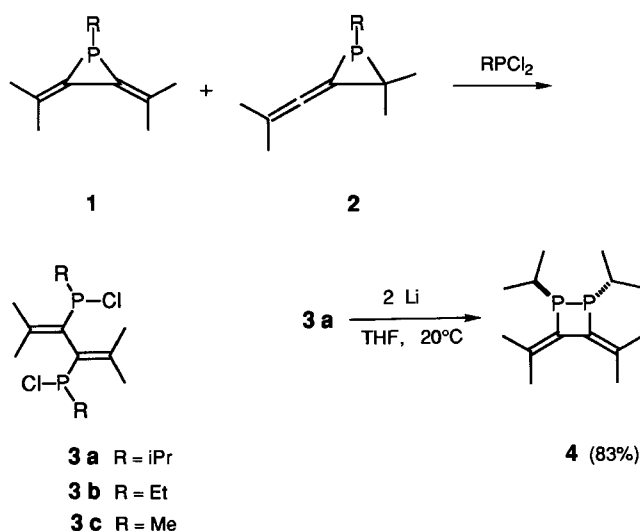
Recently, we reported on the synthesis and reactivity of "phospha[3]radialenes" **1**<sup>[4]</sup>. A fascinating ring opening of **1** and **2** with dichloroorganophosphanes exclusively provided the corresponding 2,3-bis(chlorophosphanyl)butadiene **3**<sup>[4]</sup>. In principle, **3** represents a building block in the synthesis of the 1,2-diphosphetane **4** which is accessible by reductive cyclization of **3** with an electropositive metal. However, it must be taken into account that a P–P bond can be cleaved by lithium in ethereal solvents<sup>[5]</sup>.

temperature 1,2-diisopropyl-3,4-diisopropylidene-1,2-diphosphetane (**4**) was isolated in 83% yield as a colorless, crystalline, air-sensitive compound.

The four-membered ring is indicated by the presence of long-range P,H and P,C couplings with both phosphorus atoms in the <sup>1</sup>H- and <sup>13</sup>C-NMR spectra as well as by the mass spectrum. A priori, **4** should exist as a mixture of two diastereomers (*cis/trans* isomers) caused by the two stereogenic phosphorus atoms. The NMR spectra of the crude product of the reaction of **3a** and lithium do not give any indication of the presence of two diastereomers, e.g., the <sup>31</sup>P-NMR spectrum of **4** shows only one resonance signal ( $\delta = 11.0$ )<sup>[9]</sup>. In order to ascertain unequivocally the relative configuration of **4** we determined the structure of **4** in the crystal by X-ray diffraction.

The 1,2-diphosphetane **4** exhibits *trans*-oriented isopropyl groups at the phosphorus atoms, and it adopts in the crystal a distorted nonplanar C<sub>2</sub>P<sub>2</sub> ring. The molecule possesses a 2-fold rotation axis (Figure 1). The P–P bond length [2.245(1) Å] is similar to P–P distances found in other 1,2-diphosphetanes (2.20–2.25 Å)<sup>[2,3]</sup>. The central bond of the butadiene unit [1.468(3) Å, C1–C1'] as well as

Scheme 1



When starting from **3a** the formation of the P–P bond with magnesium in THF did not occur<sup>[6]</sup>. However, when **3a** reacts with a stoichiometric amount of activated lithium<sup>[7]</sup> in THF<sup>[8]</sup> at room

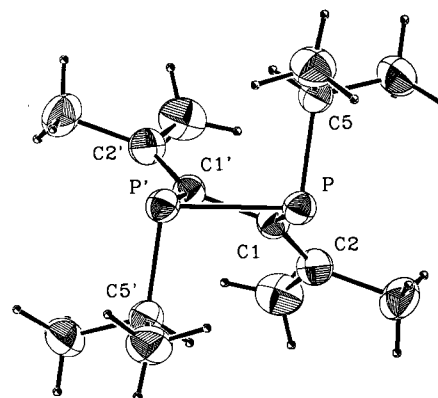


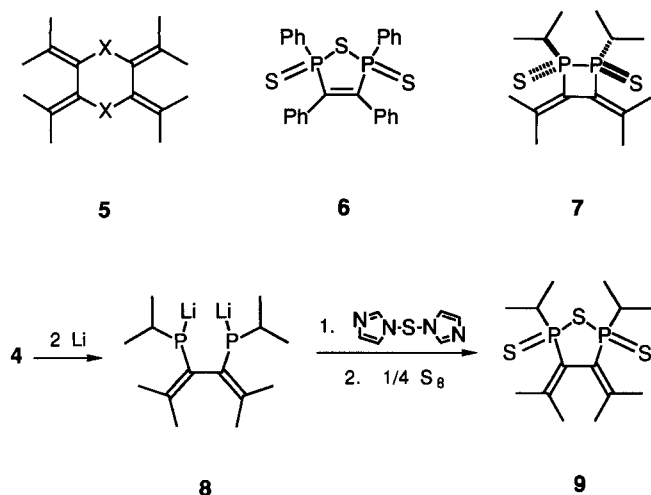
Figure 1. Molecular structure of **4** (thermal ellipsoids at the 30% probability level for P and C); selected bond lengths [Å], bond angles [°], and dihedral angles [°]: P–P' 2.245(1), P–C1 1.847(3), P–C5 1.861(3), C1–C1' 1.468(3), C1–C2 1.336(4); P'–P–C1 76.6(1), P'–P–C5 97.6(1), C1–P–C5 101.8(1), P–C1–C1' 100.1(2), P–C1–C2 125.8(2), C1'–C1–C2 132.1(2); C5–P–P'–C5' 174.7(1), C1–P–P'–C1' 15.3(1), C2–C1–C1'–C2' 57.8(3), P–C1–C1'–P' 23.2(1)

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the dihedral angle within the butadiene unit [57.8(3)°, C2–C1–C1'–C2'] are smaller than analogous bond lengths and dihedral angles of the "hetero[6]radialenes" **5**<sup>[10]</sup>. An indication of the highly strained four-membered ring is the enormous difference of *syn*-dihedral angles of the butadiene unit of **4**; the semicyclic dihedral angle (C2–C1–C1'–C2') is 34.6° larger than the endocyclic one (C1–P–P'–C1').

In contrast to 1,2-dihydro-1,2,3,4-tetraphenyl-1,2-diphosphetene<sup>[11]</sup>, which reacts with sulfur by P–P bond cleavage to the 1,2,5-thiadiphosphol derivative **6**<sup>[12]</sup>, **4** undergoes sulfuration to give the 1,2-diphosphetane **7** in 72% yield.

Scheme 2



In order to obtain an additional proof of the intact P–P bond of **7**, we synthesized a 1,2,5-thiadiphospholane **9**, a pendant of **6**. The known cleavage of P–P bonds with lithium in THF<sup>[5]</sup> makes possible the synthesis of **9** starting from the 1,2-diphosphetane **4**. **9** (18%) was readily prepared by sequential treatment of the resulting dianion **8** with diimidazolyl sulfide<sup>[13]</sup> and sulfur. According to the <sup>31</sup>P-NMR spectrum of the chromatographically purified product, **9** arises as one diastereomer.

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## Experimental

All experiments were carried out under dry Ar. – NMR: Bruker WH 400; CDCl<sub>3</sub> solutions with TMS and phosphoric acid (external standard) as reference compounds.

**1,2-Diisopropyl-3,4-diisopropylidene-1,2-diphosphetane (4):** To a stirred mixture of 17.3 g (52.9 mmol) of **3a**<sup>[4]</sup> in 100 ml of dry THF was added at room temperature in small portions 0.73 g (106 mmol) of powdered lithium (2% sodium)<sup>[7]</sup>. The mixture was sonicated until the lithium was consumed (20 min). After removal of the solvent in vacuo, condensation (80°C/0.001 Torr) afforded 11.2 g (83%) of **4**, m.p. 36–38°C. – <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ = 2.07 [sept "d", <sup>3</sup>J(H,H) = 7.0 Hz, J(P,H) + J(P',H) = 1.6 Hz, 2H, CH], 1.86 (s, 6H, =CCH<sub>3</sub>), 1.67 (s, 6H, =CCH<sub>3</sub>), 1.18 [d"t", <sup>3</sup>J(H,H) = 7.0 Hz, J(P,H) + J(P',H) = 14.8 Hz, 6H, CH<sub>3</sub>], 1.10 [d"t", <sup>3</sup>J(H,H) = 7.0 Hz, J(P,H) + J(P',H) = 14.8 Hz, 6H, CH<sub>3</sub>]. – <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ = 139.2 (s, =C), 133.2 ["t", J(P,C) + J(P',C) = 17.0 Hz, =C], 26.4 ["t", J(P,C) + J(P',C) = 8.1 Hz, CH], 22.0 ["t",

J(P,C) + J(P',C) = 18.9 Hz, CH<sub>3</sub>, double intensity], 21.2 ["t", J(P,C) + J(P',C) = 21.8 Hz, CH<sub>3</sub>], 20.4 ["t", J(P,C) + J(P',C) = 21.6 Hz, CH<sub>3</sub>]. – <sup>1</sup>H <sup>31</sup>P NMR (CDCl<sub>3</sub>): δ = 11.0 (s). – IR (film):  $\tilde{\nu}$  = 1440 cm<sup>-1</sup> (s), 1365 (s), 1150 (m). – MS (70 eV), *m/z* (%): 256 (47) [M<sup>+</sup>], 214 (40), 171 (51), 139 (43), 43 (79), 41 (100).

C<sub>14</sub>H<sub>26</sub>P<sub>2</sub> (256.3) Calcd. C 65.61 H 10.22 P 24.17  
Found C 65.35 H 10.29 P 23.74

**1,2-Diisopropyl-3,4-diisopropylidene-1,2-diphosphetane 1,2-Disulfide (7):** A mixture of 1.20 g (4.68 mmol) of **4**, 0.30 g (9.36 mmol) of sulfur, and 20 ml of benzene was stirred for 2 h at room temperature. The solvent was removed in vacuo, and crystallization from *n*-hexane gave 1.08 g (72%) of **7**, m.p. 130–132°C. – <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ = 2.69 [sept "d", <sup>3</sup>J(H,H) = 7.0 Hz, J(P,H) + J(P',H) = 2.4 Hz, 2H, CH], 2.21 ["d", J(P,H) + J(P',H) = 0.8 Hz, 6H, =CCH<sub>3</sub>], 1.76 ["d", J(P,H) + J(P',H) = 1.5 Hz, 6H, =CCH<sub>3</sub>], 1.36 [d"d", <sup>3</sup>J(H,H) = 7.0 Hz, J(P,H) + J(P',H) = 20.1 Hz, 6H, CH<sub>3</sub>], 1.23 [d"t", <sup>3</sup>J(H,H) = 7.0 Hz, J(P,H) + J(P',H) = 20.8 Hz, 6H, CH<sub>3</sub>]. – <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ = 151.2 ["t", J(P,C) + J(P',C) = 28.8 Hz, =C], 130.7 ["t", J(P,C) + J(P',C) = 92.4 Hz, =C], 29.8 ["t", J(P,C) + J(P',C) = 47.0 Hz, CH], 25.5 ["t", J(P,C) + J(P',C) = 8.8 Hz, CH<sub>3</sub>], 23.5 ["t", J(P,C) + J(P',C) = 5.7 Hz, CH<sub>3</sub>], 16.5 (s, CH<sub>3</sub>), 15.9 (s, CH<sub>3</sub>). – <sup>1</sup>H <sup>31</sup>P NMR (CDCl<sub>3</sub>): δ = 67.1 (s). – IR (film):  $\tilde{\nu}$  = 1595 cm<sup>-1</sup> (s), 1030 (s), 695 (s). – MS (70 eV), *m/z* (%): 320 (36) [M<sup>+</sup>], 278 (27), 139 (64), 91 (56), 43 (99), 41 (100).

C<sub>14</sub>H<sub>26</sub>P<sub>2</sub>S<sub>2</sub> (320.4)  
Calcd. C 52.48 H 8.18 P 19.33 S 20.01  
Found C 51.44 H 8.06 P 18.70 S 20.38

**2,5-Diisopropyl-3,4-diisopropylidene-1,2,5-thiadiphospholane 2,5-Disulfide (9):** The solution of the dianion **8**, prepared by stirring a mixture of 1.76 g (6.78 mmol) of **4**, 20 ml of THF, and 0.10 g (13.8 mmol) of powdered lithium (2% sodium)<sup>[7]</sup> for 2 h, was added within 30 min to a mixture of 1.15 g (6.92 mmol) of diimidazolyl sulfide<sup>[13]</sup> in 20 ml of benzene. After stirring for 30 min at room temperature, 0.40 g (12.5 mmol) of sulfur was added, and the mixture was heated for 10 min under reflux. Aqueous workup and chromatography (Al<sub>2</sub>O<sub>3</sub>, Activity I) with *n*-pentane followed by CH<sub>2</sub>Cl<sub>2</sub> as eluent afforded 0.44 g (18%) of **9**, m.p. 230–231°C [*n*-hexane/ethyl acetate (70:30)]. – <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ = 2.56 ["t", J(P,H) + J(P',H) = 5.9 Hz, 6H, =CCH<sub>3</sub>], 2.40 ["oct", <sup>3</sup>J(H,H) = 7.0 Hz, J(P,H) + J(P',H) = 7.0 Hz, 2H, CH], 1.88 ["t", J(P,H) + J(P',H) = 5.0 Hz, 6H, =CCH<sub>3</sub>], 1.29 [d"d", <sup>3</sup>J(H,H) = 7.0 Hz, J(P,H) + J(P',H) = 21.7 Hz, 6H, CH<sub>3</sub>], 1.21 [d"d", <sup>3</sup>J(H,H) = 7.0 Hz, J(P,H) + J(P',H) = 22.5 Hz, 6H, CH<sub>3</sub>]. – <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ = 157.1 ["t", J(P,C) + J(P',C) = 20.6 Hz, =C], 125.4 ["dd", J(P,C) + J(P',C) = 79.5 Hz, =C], 36.0 ["t", J(P,C) + J(P',C) = 54.2 Hz, CH], 26.5 (s, CH<sub>3</sub>), 22.0 (s, CH<sub>3</sub>), 16.7 (s, CH<sub>3</sub>), 14.8 (s, CH<sub>3</sub>). – <sup>1</sup>H <sup>31</sup>P NMR (CDCl<sub>3</sub>): δ = 80.8 (s). – IR (film):  $\tilde{\nu}$  = 1590 cm<sup>-1</sup> (s), 1030 (s), 685 (s). – MS (70 eV), *m/z* (%): 352 (57) [M<sup>+</sup>], 319 (21), 171 (100), 107 (72), 43 (74), 41 (79).

C<sub>14</sub>H<sub>26</sub>P<sub>2</sub>S<sub>3</sub> (352.5)  
Calcd. C 47.71 H 7.43 P 17.59 S 27.29  
Found C 47.95 H 7.81 P 17.49 S 27.45

**Crystal Structure Determination of 4**<sup>[4]</sup>: Crystals were obtained from neat **4**; crystal dimensions 0.50 × 0.45 × 0.30 mm; *a* = *b* = 857.66(7), *c* = 1983.3(4) pm; *V* = 1263.4(5) Å<sup>3</sup>; *d*<sub>calcd.</sub> = 1.010 g cm<sup>-3</sup>; *Z* = 3; space group *P*3<sub>1</sub>21; Mo-*K*<sub>α</sub> radiation; μ(Mo-*K*<sub>α</sub>) = 2.3 cm<sup>-1</sup>; Θ<sub>max</sub> = 25°, -1 ≤ *h* ≤ 10, -1 ≤ *k* ≤ 10, -23 ≤ *l* ≤ 23. 2562 reflections were measured at room temperature with a four-circle diffractometer (CAD4, Enraf-Nonius); structure solution by direct methods, hydrogen atoms located by difference Fourier analyses. Refinement with 938 independent reflections [*I* ≥ 3σ(*I*)]

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by the full-matrix method (P, C anisotropic, H isotropic) converged in the last cycle for 125 parameters at  $R = 0.0278$ ,  $R_w = 0.0265$  ( $w = 1$ ); no residual electron density larger than  $\pm 0.27 \text{ e}\text{\AA}^{-3}$ . All calculations were carried out with the system SDP<sup>[15]</sup>. Atom parameters are listed in Table 1.

Table 1. Atomic coordinates and equivalent isotropic thermal parameters [ $\text{\AA}^2$ ] for **4**;  $B_{\text{eq}} = (4/3) \cdot [a^2 \cdot B(1,1) + b^2 \cdot B(2,2) + c^2 \cdot B(3,3) + ab(\cos\gamma) \cdot B(1,2) + ac(\cos\beta) \cdot B(1,3) + bc(\cos\alpha) \cdot B(2,3)]$

Atom	X	Y	Z	$B_{\text{eq}}$
P	0.90038(9)	0.45175(9)	0.12413(4)	4.77(2)
C1	0.9142(3)	0.6662(3)	0.1483(1)	4.61(7)
C2	0.7794(3)	0.7015(4)	0.1459(1)	5.35(7)
C3	0.7837(4)	0.8563(4)	0.1829(2)	7.62(9)
C4	0.6054(4)	0.5825(4)	0.1090(2)	7.7(1)
C5	1.0649(4)	0.5240(4)	0.0536(1)	5.39(7)
C6	1.1161(4)	0.3833(5)	0.0403(2)	7.9(1)
C7	0.9820(5)	0.5624(5)	-0.0085(2)	7.5(1)

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