New Organophosphorus Ligands: 1,1,4,4-Tetrakis(diphenylphosphanyl)butatriene and Its Tetrasulfide

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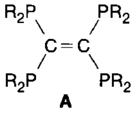
Treatment of bis(diphenylphosphanyl)ethyne with potassium diphenylphosphide in tetrahydrofuran leads to the formation of tetraphenyldiphosphane $Ph_2P{-}PPh_2$ and the title compound $(Ph_2P)_2C{=}C{=}C{=}C(PPh_2)_2$ (**1**). A mechanism is proposed for this process. Compound **1** reacts with elemental sulfur to give the tetrasulfide $[Ph_2(S)P]_2C{=}C{=}C{=}C[P(S)Ph_2]_2$ (**2**). The crystal structures of **1** and **2** have been determined by single-crystal X-ray diffraction. In both cases the linear butatriene unit shows strongly alternating C=C bond lengths as predicted in theoretical studies.

Phosphanyl-substituted alkenes and alkynes are important classes of compounds relevant as synthons and substrates to the synthesis of a variety of organophosphorus compounds and as ligands to main group and transition metals. The rigidity of the doubly and triply bonded skeleton has significant consequences regarding regio- and stereoselectivity of reactions, but also for the "ligand bite" in metal coordination. *Ethylene* molecules bearing one, two or three phosphanyl groups are well established families of polyfunctional phosphanes[1-3], but the existence of tetrakis(phosphanyl)ethylene compounds (**A**) has not yet been fully confirmed[4]. Phosphinyl-substituted *allenes* (**B**) have recently been described, however, and proved to be interesting ligands in coordination chemistry[5,6].

As part of our continuing studies in this area[1-6] we have recently become engaged in the synthesis and structural characterization of the first tetrakis(phosphanyl)*butatrienes* (**C**). Butatrienes $X_2C{=}C{=}C{=}CX_2$ with heteroatom substituents X have previously been reported for X = Cl, SR, and SiR_3[7-11], but surprisingly no analogous phosphorus species (X = PR_2) have been included in this earlier work.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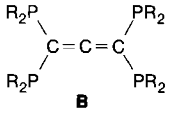
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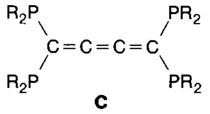
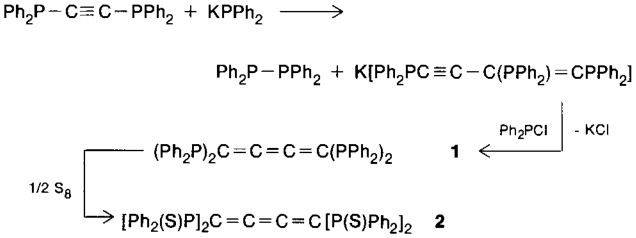

C

Synthesis, Properties, and Spectroscopic Data of 1

Bis(diphenylphosphanyl)ethyne reacts with equimolar quantities of potassium diphenylphosphide in tetrahydrofuran to give a homogeneous, deeply colored solution. Addition of equimolar quantities of chlorodiphenylphosphane to this highly reactive mixture gives tetrakis(diphenylphosphanyl)butatriene (**1**). The product is isolated as deep yellow crystals. Aqueous workup of the solution affords *trans*-1,2-bis(dichlorophosphanyl)ethene, while workup with anhydrous solvents gives tetraphenyldiphosphane.

Compound **1** is converted into the tetrasulfide **2** on treatment with elemental sulfur in dichloromethane.



The trienes **1** and **2** are readily identified by their analytical data and their NMR and mass spectra. In the proton and ^{13}C-NMR spectra the two compounds show only one set of phenyl resonances each, and the $^{31}P\{^1H\}$-NMR spectra exhibit only one single singlet with chemical shifts of $\delta = 9.7$ and 45.0 for **1** and **2**, respectively, indicating four equivalent phosphanyl groups in both molecules.

In the mass spectra (electron impact, 70 eV) the molecular ions of **1** and **2** are observed as the parent peaks M^+ at $m/z = 788$ and 916, respectively. Fragment ions are listed in the experimental section.

The spectroscopic data suggest highly symmetrical molecular structures for the two butatrienes. This conclusion has been confirmed by single-crystal X-ray structure analyses.

Crystal and Molecular Structures of 1 and 2

The two butatrienes crystallize in the monoclinic space groups $P2_1/n$ (**1**, from dichloromethane) and $P2_1/a$ (**2**, from dichloromethane/diethyl ether) with four formula units in the unit cell. Details of crystal data and structure solution are given in the experimental section and/or have been deposited.

The two molecules have no crystallographic symmetry, and even approximations to mirror or rotational symmetry

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are poorly developed. The conformation of the four diphenylphosphanyl and diphenylthiophosphanyl groups is not the same in **1** and **2**, meaning that the relative rotational positions have changed upon the addition of sulfur atoms. However, both molecules have in common a nearly planar $P_2C{=}C{=}C{=}CP_2$ skeleton with quasi-linear axes $C{=}C{=}C{=}C$ and very similar dimensions (Figures 1 and 2 and their captions).

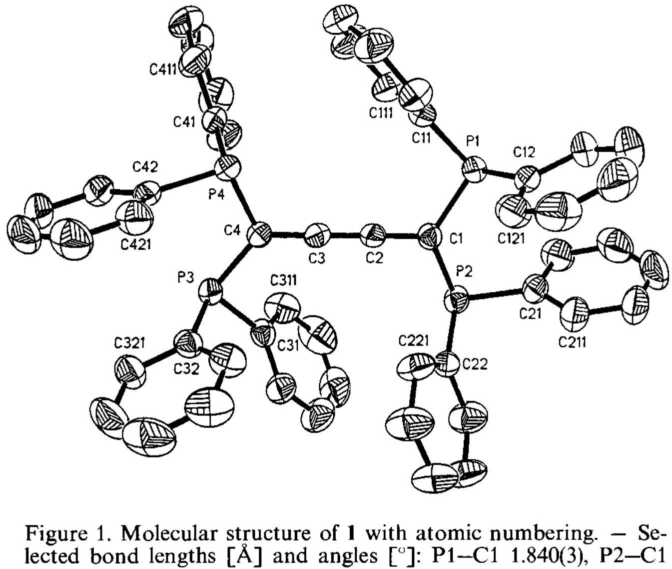

Figure 1. Molecular structure of **1** with atomic numbering. – Selected bond lengths [Å] and angles [°]: P1–C1 1.840(3), P2–C1 1.838(3), P3–C4 1.840(3), P4–C4 1.839(3), C1–C2 1.321(4), C2–C3 1.262(4), C3–C4 1.323(4); P1–C1–P2 118.9(1), P1–C1–C2 120.6(3), P2–C1–C2 118.6(3), C1–C2–C3 179.2(4), C2–C3–C4 179.5(4), P3–C4–P4 120.8(2), P3–C4–C3 121.8(3), P4–C4–C3 117.0(3). – Angle between planes: P1–P2–C1/P3–P4–C4 22.84°

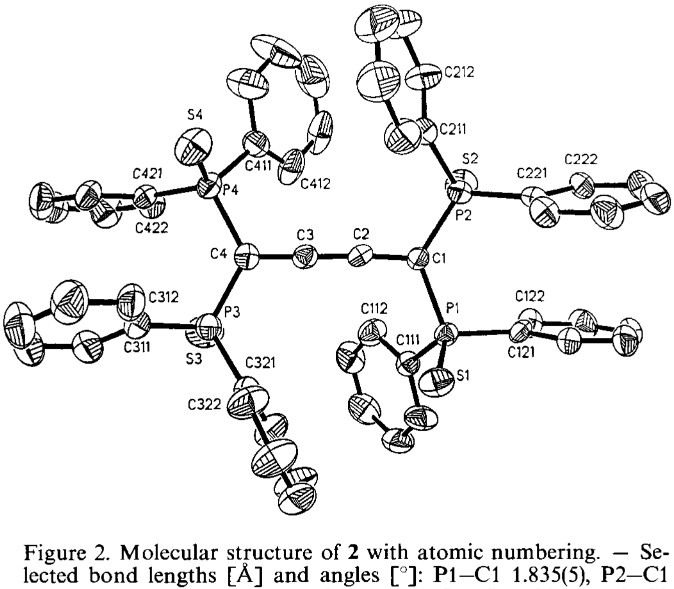

Figure 2. Molecular structure of **2** with atomic numbering. – Selected bond lengths [Å] and angles [°]: P1–C1 1.835(5), P2–C1 1.826(6), P3–C4 1.839(6), P4–C4 1.840(6), P1–S1 1.935(2), P2–S2 1.939(3), P3–S3 1.933(3), P4–S4 1.940(3), C1–C2 1.328(7), C2–C3 1.250(7), C3–C4 1.316(8); P1–C1–P2 125.3(3), P1–C1–C2 114.5(4), P2–C1–C2 119.6(4), C1–C2–C3 172.8(6), C2–C3–C4 174.3(7), P3–C4–P4 121.5(3), P3–C4–C3 119.1(4), P4–C4–C3 118.8(5). – Angle between planes: P1–P2–C1/P3–P4–C4 28.31°

The theory of chemical bonding in butatrienes is well established, and the results of the extensive calculations are in excellent agreement with experimental data. Both **1** and **2** have cumulene groups $C{=}C{=}C{=}C$ with "long/short/long" sequences of C=C bonds, which are in agreement with the literature data for other model butatrienes[12]. The $C{=}C{=}C$ angles at the two inner carbon atoms (C2, C3) are very close to 180°, and the sums of the angles at the outer carbon atoms (C1, C4) are very close to 360° indicating a planar configuration for C1 and C4. The planes P1,P2,C1 and P3,P4,C4 are inclined by 22.84° for **1** and 28.31° for **2**. The interatomic distances and angles at the diphenyl(thio)phosphanyl groups show no anomalies.

Discussion

The mechanism of the formation of product **1** in the reaction of $Ph_2P{-}C{\equiv}C{-}PPh_2$ with $KPPh_2$ in tetrahydrofuran is not yet known with certainty. Confusion arises from the fact that the nature of the (high-yield) by-products ($Ph_2P{-}PPh_2$ or *trans*-$Ph_2P{-}CH{=}CH{-}PPh_2$) depends on the procedure chosen for the addition of the reagents (sequence of reactants, dilution) and for the workup of the reaction mixture (aqueous/nonaqueous) as well as from the observation in previous studies that the use of Ph_2PH/KO*t*Bu instead of $KPPh_2$ leads to yet another product, which has been identified as the tetrakis(diphenylphosphanyl)*butadiene* $(Ph_2P)_2C{=}CH{-}CH{=}C(PPh_2)_2$[4a].

Various metalated alkynes and alkenes (and alkynyl-alkenes) are the most likely intermediates as suggested also by the results of work with the analogous poly(silyl)olefins. One of the key intermediates can be formulated as $Ph_2P{-}C^-(K^+){=}C{=}C{=}C(PPh_2)_2$ (D) or as $Ph_2P{-}C{\equiv}C{-}C^-(K^+){=}C(PPh_2)_2$ (E). The alkynyl-alkenide formula E is supported by the quenching reaction with Me_3SiCl[13] which leads to $Ph_2P{-}C{\equiv}C{-}C(SiMe_3){=}C(PPh_2)_2$, while the potassium butatrienylide(–1) (D) is the obvious precursor of **1** formed in the reaction with Ph_2PCl (above). It can be assumed, therefore, that in a first step the reagents $Ph_2PC{\equiv}CPPh_2$ and Ph_2PK give $Ph_2P{-}PPh_2$ and potassium (diphenylphosphanyl)acetylide. Attack of this new nucleophile $Ph_2P{-}C{\equiv}C^-K^+$ on $Ph_2P{-}C{\equiv}C{-}PPh_2$ then affords E/D. Work to clarify this mechanism is in progress.

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Experimental

The experiments were routinely carried out under dry, purified nitrogen. Solvents were dried, saturated with nitrogen and distilled before use. Glassware was oven-dried and filled with nitrogen. – NMR: Jeol GX 400 and 270 spectrometers. – MS: Varian MAT 311A.

1,1,4,4-Tetrakis(diphenylphosphanyl)butatriene (**1**): A solution of bis(diphenylphosphanyl)ethyne (4.93 g, 12.5 mmol) in tetrahydrofuran (100 ml) was treated with a 0.5 M solution of potassium diphenylphosphide in THF (25 ml, 12.5 mmol). The mixture was heated to reflux for 3.5 h, subsequently cooled to 0°C, and a solution of chlorodiphenylphosphane (2.25 g, 12.5 mmol) in THF (75 ml) was added dropwise with stirring. Stirring was continued at 20°C for 12 h and the solvent removed in vacuo. The solid residue was treated with ethanol (200 ml) and the undissolved yellow solid collected, washed with water (50 ml), dried in vacuo, and crystallized from dichloromethane; yellow crystals, 1.62 g (33%), m.p. 220°C. − ^{1}H NMR ($CDCl_3$): δ = 7.08−7.56 (m, Ph). − ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 127.9 [m, C_m], 128.2 [t, J(P,C) = 3.7 Hz, CP_2], 128.6 (s, C_p), 133.9−134.1 (m, C_o, C_{ipso}), 135.9 [tt, J(P,C) = 5.5 and 1.8 Hz, =C=]. − ^{31}P{^{1}H} NMR ($CDCl_3$): δ = 9.7 (s). − MS (EI, 70 eV), *m/z* (%): 788 (11) [M^+], 603 (71) [M^+ − PPh_2], 185 (100) [PPh_2^+]. − $C_{52}H_{40}P_4$ (788.8): calcd. C 79.18, H 5.11, P 15.71; found C 78.59, H 5.36, P 15.57.

1,1,4,4-Tetrakis(diphenylthiophosphinyl)butatriene (**2**): Compound **1** (0.20 g, 0.25 mmol) was dissolved in dichloromethane (25 ml) and elemental sulfur was added (0.1 g, excess). The mixture was stirred for 2 h, undissolved sulfur was removed by filtration, and the solvent was evaporated in vacuo. The residue was crystallized from dichloromethane/diethyl ether (1:1); red-brown crystals, 0.21 g (90% yield), m.p. 208°C. − ^{1}H NMR ($CDCl_3$): δ = 7.16−7.52 (m, Ph). − ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 127.8−132.3 (m). − ^{31}P{^{1}H} NMR ($CDCl_3$): δ = 45.03 (s). − MS (CI), *m/z* (%): 916 (1.6) [M^+], 884 (13.1) [M^+ − S], 852 (9.4) [M^+ − 2 S], 820 (2.9) [M^+ − 3 S], 788 (2.0) [M^+ − 4 S], 588 (100). − $C_{52}H_{40}P_4$ (917.05): calcd. C 68.10, H 4.39, S 13.99; found C 68.14, H 4.28, S 14.19.

Crystallographic Structure Determinations: Crystals in glass capillaries, Enraf-Nonius CAD-4 diffractometer, 23°C, graphite-monochromated Mo-K_α radiation (λ = 0.71069 Å), ω and Θ-2Θ scan mode for **1** and **2**, respectively. Lp corrections applied, but intensity data not corrected for absorption effects. Structures solved by direct methods (SHELXTL-PLUS) and completed by difference Fourier syntheses (SHELXTL-PLUS).

1: $C_{52}H_{40}P_4$, M_r = 788.79, monoclinic, a = 11.589(1), b = 15.689(1), c = 23.631(1) Å, β = 102.96(1)°, space group $P2_1/n$, Z = 4, D_{calc} = 1.251 g cm^{-1}, F(000) = 1648, μ(Mo-K_α) = 2.1 cm^{-1}. 9624 intensity data measured up to $(\sin\Theta/\lambda)_{max}$ = 0.64 Å^{-1}. 5238 independent structure factors considered "observed" [$F_o \geq 4\sigma(F_o)$] and used for refinement. All hydrogen atoms calculated and fixed in idealized geometrical positions. Non-hydrogen atoms refined with anisotropic displacement parameters; function minimized was $\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2]^{1/2}$, $w = 1/\sigma^2(F_o)$. R (R_w) = 0.056 (0.054) (number of refined parameters: 505). Residual electron density: +0.45/−0.28 eÅ^{-3}.

2: $C_{52}H_{40}P_4S_4$, M_r = 917.03, monoclinic, a = 17.977(1), b = 12.565(1), c = 20.660(1) Å, β = 99.09(1)°, space group $P2_1/a$, Z = 4, D_{calc} = 1.322 g cm^{-1}, F(000) = 1904, μ(Mo-K_α) = 3.7 cm^{-1}. 7784 intensity data measured up to $(\sin\Theta/\lambda)_{max}$ = 0.57 Å^{-1}. 4041 independent structure factors considered "observed" [$F_o \geq 3\sigma(F_o)$] and used for refinement. All hydrogen atoms located and included in the refinement with fixed isotropic displacement parameters (U_{iso} = 0.05 Å^2). Non-hydrogen atoms refined with anisotropic displacement parameters; function minimized was $\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2]^{1/2}$, $w = 1/\sigma^2(F_o)$. R (R_w) = 0.052 (0.052) (number of refined parameters: 541). Residual electron density: +0.40/−0.27 eÅ^{-3}.

Further information on the X-ray structure determinations may be obtained from Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, on quoting the depository number CSD-57497, the names of the authors, and the journal citation.

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[1] [1a] H. Schmidbaur, R. Herr, J. Riede, *Chem. Ber.* **1984**, *117*, 2322−2326. − [1b] H. Schmidbaur, R. Herr, G. Müller, J. Riede, *Organomet.* **1985**, *4*, 1208−1214.

[2] [2a] H. Schmidbaur, K. Dziwok, G. Reber, G. Müller, *Helv. Chim. Acta* **1987**, *70*, 1905−1910. − [2b] H. Schmidbaur, A. Schier, G. Reber, G. Müller, *Inorg. Chim. Acta* **1988**, *147*, 143−150, and references therein.

[3] H. Schmidbaur, C. M. Frazao, G. Reber, G. Müller, *Chem. Ber.* **1989**, *122*, 259−263.

[4] [4a] H. Schmidbaur, C. Paschalidis, O. Steigelmann, D. L. Wilkinson, G. Müller, *Chem. Ber.* **1989**, *122*, 1857−1861. − [4b] H. Schmidbaur, C. Paschalidis, G. Reber, G. Müller, *Chem. Ber.* **1988**, *121*, 1241−1254, and references therein.

[5] [5a] H. Schmidbaur, T. Pollok, G. Reber, G. Müller, *Chem. Ber.* **1987**, *120*, 2015−2022. − [5b] H. Schmidbaur, T. Pollok, G. Reber, G. Müller, *Chem. Ber.* **1987**, *120*, 1403−1412.

[6] H. Schmidbaur, R. Herr, T. Pollok, A. Schier, G. Müller, J. Riede, *Chem. Ber.* **1985**, *118*, 3105−3113.

[7] B. Heinrich, A. Roedig, *Angew. Chem.* **1968**, *80*, 367−377; *Angew. Chem. Int. Ed. Engl.* **1968**, *7*, 375−376.

[8] [8a] A. Roedig, G. Zaby, *Tetrahedron Lett.* **1977**, *21*, 1771−1772. − [8b] A. Roedig, G. Zaby, W. Scharf, *Chem. Ber.* **1977**, *110*, 1484−1491.

[9] [9a] J. R. Fritch, K. P. C. Vollhardt, M. R. Thompson, V. D. Day, *J. Am. Chem. Soc.* **1979**, *101*, 2768−2770. − [9b] J. R. Fritch, K. P. C. Vollhardt, *Isr. J. Chem.* **1985**, *26*, 131−135.

[10] [10a] T. Kusumoto, T. Hiyama, *Tetrahedron Lett.* **1987**, *28*, 1807−1810. − [10b] T. Kusumoto, T. Hiyama, *Tetrahedron Lett.* **1987**, *28*, 1811−1812. − [10c] T. Kusumoto, T. Hiyama, *Bull. Chem. Soc. Jpn.* **1990**, *63*, 3103−3110. − [10d] Y. Morimoto, Y. Higuchi, K. Wakamatsu, K. Oshima, K. Utimoto, N. Yasuoka, *Bull. Chem. Soc. Jpn.* **1989**, *62*, 639−641.

[11] S. A. Petrich, Y. Pang, V. G. Young, T. J. Barton, *J. Am. Chem. Soc.* **1993**, *115*, 1591−1593.

[12] [12a] Z. Berkovitch-Yellin, L. Leiserowitz, *Acta Crystallogr., Sect. B*, **1977**, *33*, 3657−3669. − [12b] H. Irngartinger, H.-U. Jäger, *Angew. Chem.* **1976**, *88*, 615−616; *Angew. Chem. Int. Ed. Engl.* **1976**, *15*, 562−563.

[13] H. Schmidbaur, S. Manhart, unpublished results, **1993**.

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