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New Organophosphorus Ligands: 1,1,2-Tris(diphenylphosphanyl)cyclopropane and Its Derivatives

Hubert Schmidbaur*, Stefan Manhart, and Annette Schier

Anorganisch-chemisches Institut der Technischen Universität München,
Lichtenbergstraße 4, D-85748 Garching

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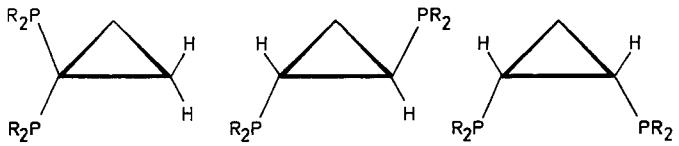
Cyclopropanation of 1,1,2-tris(diphenylphosphanyl)ethene with dimethylsulfonium methylide affords the title compound **1**. The trifunctional phosphane is transformed into the trioxide **2** and trisulfide **3** by oxidation with hydrogen peroxide or elemental sulfur, respectively. With the tetrahydrofuran–borane complex the tris(phosphane–borane) **4** is obtained. The crystal structure of compound **1** has been determined by single-crystal X-ray diffraction.

Organophosphanes have found widespread applications as substrates and synthons in synthesis and as ligands in coordination chemistry and catalysis. Recent studies have focused on the stereochemistry of phosphanes and the consequences for the stereo- and regioselectivity of their reactions. Chiral phosphanes based on various structural prerequisites are of growing interest in this context.

The rigid cyclopropane ring offers a choice of stereochemically interesting substitution patterns, which have not been exploited for designing multifunctional phosphanes. Geminal substitution with phosphanyl substituents leads to 1,3-bidentate compounds **A**[1,2], while vicinal substitution gives a pair of 1,4-bidentate species $\mathbf{B}_1$, $\mathbf{B}_2$[3], only one of which can normally function as a chelating ligand. No higher phosphane functionality has been reported for cyclopropanes. We now describe the synthesis, structure, and properties of a 1,1,2-trisubstituted cyclopropane, where both geminal and (*cis*/*trans*) vicinal functionality are available in the same molecule.



Synthesis of the Phosphane 1 and its Derivatives

1,1,2-Tris(diphenylphosphanyl)ethene has recently been prepared by a convenient high-yield synthesis[4]. This olefin can be converted into the corresponding cyclopropane **1** by treatment with dimethylsulfonium methylide prepared in situ from trimethylsulfonium iodide and *n*-butyllithium.

$$(Ph_2P)_2C{=}CH(PPh_2) + [Me_2S{=}CH_2] \longrightarrow Me_2S + (Ph_2P)_2C(\text{—}CH_2\text{—})CH(PPh_2)$$

1

Its composition is confirmed by elemental analysis and mass spectrometry. ^{1}H-, ^{13}C-, and ^{31}P-NMR spectroscopy are employed for further identification.

Compound **1** can be oxidized with aqueous hydrogen peroxide in tetrahydrofuran to the *P*,*P*′,*P*″-trioxide **2**. The reaction with elemental sulfur gives the *P*,*P*′,*P*″-trisulfide **3**.

$$\mathbf{1} + 3\,H_2O_2 \longrightarrow 3\,H_2O + \mathbf{2}$$

$$\mathbf{1} + 3/8\,S_8 \longrightarrow \mathbf{3}$$

$$\mathbf{1} + 3\,H_3B \cdot OC_4H_8 \longrightarrow 3\,C_4H_8O + \mathbf{4}$$

2: X = O
3: X = S
4: X = BH_3

$[Ph_2(X)P]_2C(\text{—}CH_2\text{—})CH[P(X)Ph_2]$

A tris(phosphane–borane) compound **4** is obtained by the reaction of **1** with the monoborane–tetrahydrofuran complex.

All three compounds are colorless crystalline materials, stable to air and water, and soluble in polar organic solvents. Analytical and spectroscopic data are summarized in the experimental section.

Crystal Structure of Compound 1

The compound crystallizes from methanol as colorless, triclinic crystals (space group $P\bar{1}$, Nr. 2 Internat. Tables), with a pair of enantiomers in the unit cell. The two optical isomers are related to each other by a center of inversion. The molecular structure is shown in Figure 1, with selected bond distances and angles given in the caption.

Owing to the unsymmetrical substitution pattern, the cyclopropane ring has three different C–C bond lengths [1.548(3), 1.512(3), and 1.495(4) Å], which compare well with the data of the equilateral geometry of the unsubstituted cyclopropane molecule [1.501(2) Å]. The angle P1–C1–P2 = 114.8(1)° is smaller than the P–C–P angle found in 1,1-bis(diphenylphosphanyl)cyclopropane [118.0(2)°][1], but comparable to the standard H–C–H angles of unsubstituted cyclopropane (115°).

Regarding the ligand properties of compound **1**, the relative orientation of the Ph_2P donor function is of special interest. The lone pairs of electrons at the geminal phosphane substituents (P1, P2) point in opposite directions, similar to the situation found[1] in 1,1-$(Ph_2P)_2C_3H_4$, and therefore metal complexation with formation of

four-membered rings would require a full P–C bond rotation into a conformation amenable to chelation. The lone pairs at the *cis*-vicinal phosphorus atoms P1 and P3, however, are clearly oriented in such a way, that metal chelation is possible without any change of conformation of ligand **1**. The configuration is thus comparable to that of $(Ph_2P)_2C{=}CH(PPh_2)$[4], but slightly smaller valence angles appear to make **1** a particularly suitable chelating ligand for medium-sized soft transition metals.

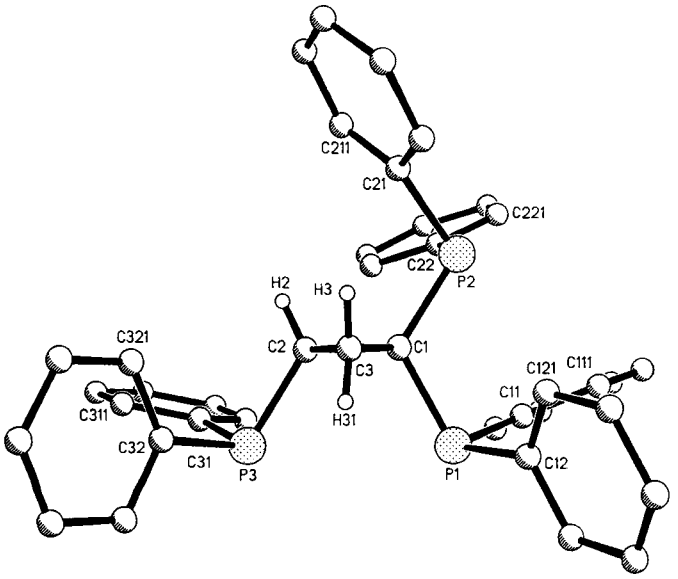


Figure 1. Molecular structure of **1** with atomic numbering. Selected bond lengths [Å] and angles [°]: C1–C2 1.548(3), C1–C3 1.512(3), C2–C3 1.495(4), P1–C1 1.858(2), P1–C11 1.832(3), P1–C12 1.833(3), P2–C1 1.844(3), P2–C21 1.838(3), P2–C22 1.831(3), P3–C2 1.827(3), P3–C31 1.838(3), P3–C32 1.835(3); P–C1–P2 114.8(1), P1–C1–C2 117.4(2), P2–C1–C2 123.0(2), P1–C1–C3 112.9(2), P2–C1–C3 117.7(2), C2–C1–C3 58.5(2), P3–C2–C1 123.1(2), P3–C2–C3 114.3(2), C1–C2–C3 59.6(2), C1–C3–C2 62.0(2), C1–P1–C11 103.9(1), C1–P1–C12 102.3(1), C11–P1–C12 100.4(1), C1–P2–C21 103.7(1), C1–P2–C22 104.9(1), C21–P2–C22 103.0(1), C3–P3–C31 102.6(1), C2–P3–C32 99.9(1), C31–P3–C32 103.1(1)

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Experimental

All experiments were carried out under dry nitrogen. Solvents were dried, distilled and saturated with nitrogen. Glassware was oven-dried and filled with nitrogen. – NMR: Jeol GX 270 spectrometer. – MS: Varian MAT 311A. – IR: Nicolet FX 354.

1,1,2-Tris(diphenylphosphanyl)cyclopropane (**1**): A slurry of trimethylsulfonium iodide (24.5 g, 120 mmol) in tetrahydrofuran (150 ml) is treated at 0°C with a solution of *n*-butyllithium in hexane (72.3 ml, 1.66 M) during a period of 10 min with stirring. After another 10 min of vigorous agitation a solution of 1,1,2-tris(diphenylphosphanyl)ethene (17.12 g, 29.41 mmol) in THF (100 ml) is added dropwise, and stirring is continued at 0°C for 30 min, at 20°C for 90 min, and finally at reflux temperature for 2 h. After cooling to ambient temp. the reaction mixture is filtered, and the solvents are removed from the filtrate in vacuo. The viscous oily residue is crystallized from methanol; colorless crystals (7.7 g, 44%), m.p. 139°C. – ^{1}H NMR (C_6D_6): δ = 1.26–1.49 (m, 2H, CH_2), 1.96–2.02 (m, 1H, CH), 6.71–7.93 (m, 30H, Ph). – $^{13}C\{^1H\}$ NMR (C_6D_6): δ = 17.73 [ddd, J(P,C) = 66.4, 24.4, and 8.0 Hz, CP_2], 20.36 [dd, J(P,C) = 14.0 and 5.0 Hz, CH_2], 24.33 [td, J(P,C) = 14.5 and 2.3 Hz, CHP], 127.65–141.02 (m, Ph). – $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 161.83 [dd, J(P,P) = 148.3 and 9.9 Hz, P], –0.79 [dd, J(P,P) = 9.9 and 4.2 Hz, P], 10.69 [dd, J(P,P) = 148.3 and 4.2, P]. – MS (EI, 70 eV), *m/z* (%): 594.4 (37) [M^+], 517.2 (13) [M^+ – Ph], 409.3 (100) [M^+ – PPh_2]. – $C_{39}H_{33}P_3$ (594.6): calcd. C 78.78, H 5.59; found C 78.78, H 5.31.

1,1,2-Tris(diphenylphosphinoyl)cyclopropane (**2**): A solution of **1** (0.68 g, 1.14 mmol) in THF (10 ml) is treated at 0°C with aqueous hydrogen peroxide (1 ml, 33%) with stirring. The mixture is warmed to ambient temp. and agitated for another 30 min. The solvents are then removed in vacuo at 100°C. Colorless crystals remain (0.65 g, 89%), m.p. 145°C. – ^{1}H NMR ($CDCl_3$): δ = 1.9–2.1 (m, 1H, CH), 2.2–2.35 (m, 1H, CH), 2.4–2.55 (m, 1H, CH), 6.9–8.2 (m, 30H, Ph). – $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 16.1 (s, broad, CH_2), 22.7 [d, broad, J(P,C) = 94.7 Hz, CHP], 27.0 [ddd, J(P,C) = 74.4, 69.7, and 4.6 Hz, CP_2], 127.3–134.9 (Ph signals). – $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 25.6 [dd, J(P,P) = 10.9 and 8.7 Hz, P], 31.6 [dd, J(P,P) = 21.8 and 10.9 Hz, P], 35.6 [dd, J(P,P) = 21.8 and 8.7 Hz, P]. – MS (CI, negative ions), *m/z* (%): 642.3 (16) [M^-], 457.2 (100) [M^- – PPh_2], 441.2 (6) [M^- – $POPh_2$], 217.1 (50) [$PO_2Ph_2^-$]. – $C_{39}H_{33}O_3P_3$ (642.4): calcd. C 72.89, H 5.18; found C 72.93, H 5.37.

1,1,2-Tris(diphenylthiophosphinoyl)cyclopropane (**3**): A solution of **1** (0.42 g, 0.71 mmol) in THF (10 ml) is treated with elemental sulfur (0.10 g, 3.13 mmol) at 20°C. After 30 min of stirring nonreacted sulfur is filtered and the product is precipitated from the filtrate by the addition of ethanol (30 ml). A white powder is obtained after filtration and drying in vacuo (0.41 g, 83%), m.p. 223°C. – ^{1}H NMR (CD_2Cl_2): δ = 2.12–2.29 (m, 1H, CH), 2.39–2.56 (m, 1H, CH), 2.89–3.05 (m, 1H, CH), 6.90–8.05 (m, 30H, Ph). – $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ = 21.45 (s, broad, CH_2), 27.60 [dd, J(P,C) = 73.5 and 3.2 Hz, CHP], 32.45 [ddd, J(P,C) = 46.4, 41.8, and 6.0 Hz, CP_2], 125.9–135.3 (Ph resonances). – $^{31}P\{^1H\}$ NMR (CD_2Cl_2): 39.81 [dd, J(P,P) = 10 and 4.3 Hz, P], 47.56 [dd, J(P,P) = 17.4 and 10.0 Hz, P], 57.56 [d, broad, J(P,P) = 17.4 Hz, P]. – MS (CI, positive ions), *m/z* (%): 691.4 (17) [MH^+], 659.4 (17) [MH^+ – S], 475.3 (10) [MH^+ – PPh_2S], 461.3 (100) [MH^+ – $CHPh_2S$]. – $C_{39}H_{33}P_3S_3$ (690.85): calcd. C 67.81, H 4.81, P 13.45; found C 67.66, H 4.76, P 13.37.

1,1,2-Tris(boranatodiphenylphosphonio)cyclopropane (**4**): A solution of **1** (0.77 g, 1.3 mmol) in THF (20 ml) is treated with a solution of borane–tetrahydrofuran in THF (3.9 ml, 1.0 M) at 0°C. After 12 h at 20°C the solvent is removed from the reaction mixture, the residue is taken up in chloroform, and the product precipitated by the addition of pentane. A colorless solid is obtained (0.63 g, 76%), m.p. 180°C. – ^{1}H NMR ($CDCl_3$): δ = 0.5–2.0 [m, broad, J(B,H) ca. 75 Hz, 9H, BH_3], 2.08–2.28 (m, 2H, CH_2), 2.64–3.02 (m, 1H, CH), 6.85–7.96 (m, 30H, Ph). – $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 19.84 [ddd, J(P,C) = 21.7, 18.7, and 3.2 Hz, CP_2], 20.33 (s, broad, CH_2), 22.0 [d, broad, J(P,C) = 40.0 Hz, CHP], 124.7–135.6 (Ph resonances). – $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 21.77, 29.38, and 37.99 (s, quadrupole broadened). – MS (CI, positive ions), *m/z* (%): 637.7 (12) [MH^+], 611.6 (27) [MH^+ – 2 BH_3], 595.6 (100) [MH^+ – 3 BH_3]. – IR (KBr): ν = 2388 cm^{-1} (νBH).

Crystallographic Structure Determination of Compound **1**: Tris(phosphane) **1** was mounted in a glass capillary on an Enraf-Nonius CAD-4 diffractometer (graphite-monochromated Mo-K_α radiation, L = 0.71069 Å; Θ-Θ scan mode, 20°C). An Lp correction was applied, but intensity data were not corrected for absorption effects. The structure was solved by direct methods (SHELXTL-PLUS) and completed by difference Fourier syntheses. **1**, $C_{39}H_{33}P_3$, M_{rel} =

594.62, triclinic, $a = 9.907(1)$, $b = 10.506(1)$, $c = 16.807(1)$ Å, $\alpha = 89.29(1)$, $\beta = 80.87(1)$, $\gamma = 66.63(1)^\circ$, space group $P\bar{1}$ (Nr. 2), $Z = 2$, $D_{calc} = 1.247$ gcm^{-3}, $F(000) = 624$, $\mu(\text{Mo-}K_\alpha) = 2.1$ cm^{-1}. 5536 intensity data were measured up to $(\sin\Theta/\lambda)_{max} = 0.59$ Å^{-1}, of which 4215 independent structure factors were considered "observed" ($F_o \geqslant 4\sigma F_o$) and used for refinement. The non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms could be located. The cyclopropane hydrogen atoms were refined isotropically, while the phenyl hydrogen atoms were included with fixed isotropic displacement parameters [$U_{iso(fix)} = 0.05$ Å^3]. The function minimized was $\Sigma w(|F_o| - |F_c|)^2/\Sigma w F_o^2]^{1/2}$, $w = 1/\sigma^2 \cdot (F_o)$. The final R (R_w) values were 0.043 (0.037). Number of refined parameters: 391, residual electron density: +0.33/−0.28 eÅ^{-3}. Further information may be obtained from Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, on quoting the depository number CSD-57492, the names of the authors and the journal citation.

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