# New Organophosphorus Ligands: Cyclopropanation and Other Reactions of Cumulenes Bearing Diphenylphosphanyl Substituents

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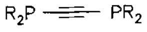
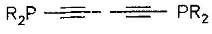
Hydrophosphorylation of 1,4-bis(diphenylphosphanyl)butadiyne with diphenylphosphane leads to the butadiene $(Ph_2P)_2C{=}CH{-}CH{=}C(PPh_2)_2$ (**1**). Treatment of **1** with dimethylsulfonium methylide gives the vinylcyclopropane $(Ph_2P)_2C{=}CH{-}CH(CH_2)C(PPh_2)_2$ (**2**). Compound **2** reacts with aqueous hydrogen peroxide, elemental sulfur, or selenium to afford the tetrachalcogenides $(Ph_2XP)_2C{=}CH{-}CH(CH_2)C(PXPh_2)_2$ with X = O (**3**), X = S (**4**), X = Se (**5**), respectively. While the tetraphosphane **1** and the vinylcyclopropane compound **2** cannot be converted into a bis(cyclopropyl) compound with an excess of $Me_2S{=}CH_2$, the tetrasulfide **4** readily affords a mixture of (1*R*,1'*R*)-/(1*S*,1'*S*)- and *meso*-2,2,2',2'-tetrakis(diphenylthiophosphinyl)-1,1'-bicyclopropyl (**6**, **7**) in good yield. Treatment of 1,1,4,4-tetrakis(diphenylphosphanyl)butatriene with dimethylsulfonium methylide leads to the vinylidenecyclopropane $(Ph_2P)_2C{=}C{=}C(CH_2)C(PPh_2)_2$ (**8**). Compound **8** is converted into its tetrasulfide $(Ph_2SP)_2C{=}C{=}C(CH_2)C(PSPh_2)_2$ (**9**) by treatment with elemental sulfur. The crystal structures of **1**, **2**, **4**, **7**, and **8** have been determined by single-crystal X-ray diffraction.

Phosphanyl-substituted organic molecules are important classes of compounds relevant as synthons and substrates for the synthesis of a variety of organophosphorus reagents and as ligands to main group and transition metals. In polyfunctional phosphanes, the individual functional groups may be involved in classical reactions quite independently, if the organic skeleton is stereochemically flexible, as for example in α,ω-bis(phosphanyl)alkanes. For polyphosphanyl compounds based on a rigid skeleton, however, the structural situation has interesting consequences: Reactivity can be limited to a certain regio- and stereoselectivity, and for metal coordination a definite "ligand bite" can be tailored. Polyphosphanylalkynes[1,2] **A**, **B**, ethylenes[3–6] **C**, **D**, **E**, **F**, cyclopropanes[7–10] **G**, **H**, **I**, **J**, allenes[11,12] **K**, **L**, **M**, and other cumulenes[13] **N** are examples in case.

For the olefins, it is immediately obvious that the substitution pattern (*gem*, *E*, *Z*) determines whether the molecule can function as a chelating ligand or not, and that ambidentate chelation with different "bites" can be accomplished.

The stereochemistry of polyphosphanyl*cyclopropanes* also offers a variety of ligand properties predetermined by the position of the substituents. As a continuation of our previous studies[10,13] we now extended our investigations to vinyl-substituted cyclopropane and finally bis(cyclopropyl) molecules. It was expected that the recently synthesized poly(phosphanyl)butadienes, -allenes and -butatrienes should offer a convenient route to these target molecules. Cyclopropanation of the corresponding monoolefins has already been demonstrated to give access to mono-cyclopropyl-based phosphanes[7–10].


**A**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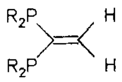
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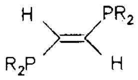
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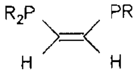
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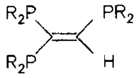
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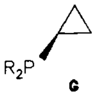
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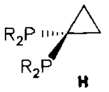
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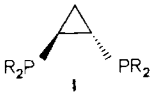
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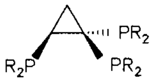
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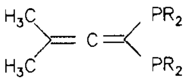
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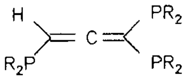
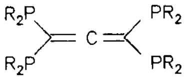

**L**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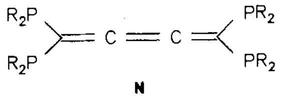
**N**

Polyene and polyyne compounds are also of current interest in polymer and material science[14,15]. Given the situation that presently only very few phosphanyl-substituted olefins and alkynes are available as monomers, the results of the present study are also relevant to the development of a chemistry of phosphanyl-substituted polymers.

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### A Rational Synthesis of 1,1,4,4-Tetrakis(diphenylphosphanyl)-1,3-butadiene (1)

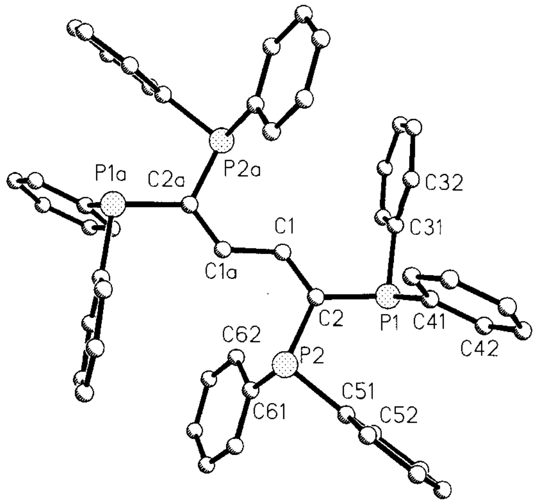
The title compound **1** has been obtained previously as an unexpected minor byproduct of the synthesis of tris(diphenylphosphanyl)ethene by $Ph_2PH$ addition to $Ph_2PC{\equiv}CPPh_2$[6]. In the absence of a plausible mechanism for its formation, an erroneous structure was initially proposed, which was only corrected after the determination of the crystal structure of the tetrasulfide derivative. A new route to the synthesis of **1** has now been found in the hydrophosphorylation of 1,4-bis(diphenylphosphanyl)-1,3-butadiyne[2] with two equivalents of diphenylphosphane. The reaction gives **1** in virtually quantitative yield (Eq. 1). The analytical and spectroscopic data are in full agreement with the data reported previously[6].

$$Ph_2PC\equiv C-C\equiv CPPh_2 \quad + \quad 2\ HPPh_2 \longrightarrow \underset{\mathbf{1}}{(Ph_2P)_2C{=}CH{-}CH{=}C(PPh_2)_2} \qquad \text{(Eq. 1)}$$

### Crystal and Molecular Structure of 1

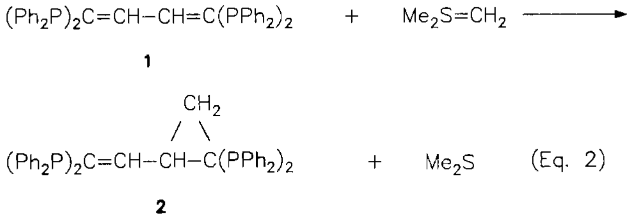
The butadiene **1** crystallizes from dichloromethane as bright yellow, triclinic crystals (space group $P\bar{1}$) with one molecule in the unit cell. The molecule exhibits the *single-trans* or *E* configuration with an inversion centre between the butadiene carbon atoms C2 and C3 (crystallographic numbering: C1, C1a, Figure 1). The C–C bond lengths of the butadiene skeleton [C1–C2 = 1.341(3), C1–C1a = 1.441(5) Å] are comparable with those of unsubstituted butadienes[16]. The sum of the angles at C2 is very close to 360° indicating a planar configuration for this carbon atom. The angle P1–C2–P2 = 119.3(1)° is comparable with the P1–C1–P2 angle of 1,1-bis(diphenylphosphanyl)ethene [119.0(3)°][3a]. These and other selected bond lengths and angles are presented in the caption to Figure 1.

Figure 1. Molecular structure of 1,1,4,4-tetrakis(diphenylphosphanyl)-1,3-butadiene (**1**) in the crystal (phenylhydrogen atoms of all structures of **1**, **2**, **4**, **7**, and **8** have been omitted for clarity). – Selected bond lengths [Å] and angles [°]: C1–C2 1.341(3), C1–C1a 1.441(5), C2–P1 1.834(2), C2–P2 1.835(2); C1a–C1–C2 126.6(3), P2–C2–P1 119.3(1), C1–C2–P1 122.4(2), C1–C2–P2 118.2(2)



### Cyclopropanation of the Butadiene 1

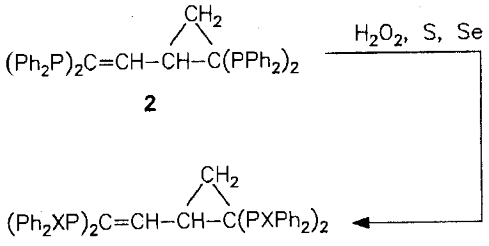
Butadiene **1** can be converted into the corresponding tetrakis(diphenylphosphanyl)vinylcyclopropane **2** by treatment with dimethylsulfonium methylide prepared in situ from trimethylsulfonium iodide and *n*-butyllithium (Eq. 2). Even with a large excess of dimethylsulfonium methylide, only one double bond undergoes cyclopropanation. Regarding the chirality as controlled by the configuration at C3, both enantiomers (*R* and *S*) are obtained in a 1:1 ratio. The product was isolated as a white solid, m.p. 223°C, soluble in tetrahydrofuran, $CH_2Cl_2$, $CHCl_3$, benzene, and toluene. It is stable to air and moisture.



$$\underset{\mathbf{1}}{(Ph_2P)_2C{=}CH{-}CH{=}C(PPh_2)_2} + Me_2S{=}CH_2 \longrightarrow \underset{\mathbf{2}}{(Ph_2P)_2C{=}CH{-}\overset{CH_2}{\overset{/\ \backslash}{CH{-}C}}(PPh_2)_2} + Me_2S \qquad \text{(Eq. 2)}$$

Compound **2** was readily identified by elemental analysis and by its mass and NMR spectra. The $^{31}P\{H\}$-NMR spectrum shows four singlet resonances with chemical shifts of $\delta = -12.32, -5.68, -1.82$, and $6.99$ indicating four nonequivalent phosphanyl groups. In the $^{13}C$- and $^1H$-NMR spectra, singlet signals with chemical shifts typical of a vinylcyclopropane skeleton are observed, together with complex phenyl multiplet resonances (see Experimental).

Compound **2** can be oxidized with aqueous hydrogen peroxide in tetrahydrofuran to give the tetraoxide **3** (Eq. 3). The reactions with elemental sulfur or selenium give the tetrasulfide **4** (Eq. 4) and the tetraselenide **5** (Eq. 5), respectively.



$$\underset{\mathbf{2}}{(Ph_2P)_2C{=}CH{-}\overset{CH_2}{\overset{/\ \backslash}{CH{-}C}}(PPh_2)_2} \xrightarrow{H_2O_2,\ S,\ Se} (Ph_2XP)_2C{=}CH{-}\overset{CH_2}{\overset{/\ \backslash}{CH{-}C}}(PXPh_2)_2$$

(Eq. 3) **3** : X = O

(Eq. 4) **4** : X = S

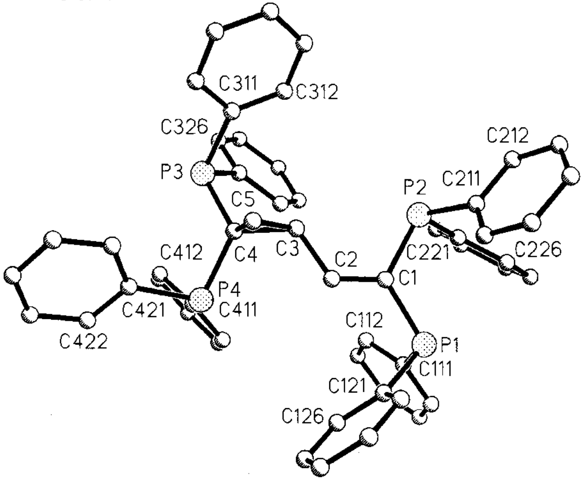
(Eq. 5) **5** : X = Se

The derivatives **3**–**5** are colorless crystalline materials, stable to air and moisture and soluble in polar organic solvents. Their analytical and spectroscopic data are summarized in the experimental section.

### Crystal and Molecular Structure of the Vinylcyclopropane 2 and its Tetrasulfide 4

The vinylcyclopropane **2** and its tetrasulfide **4** crystallize from dichloromethane/pentane as colorless, monoclinic crystals (space group $P2_1/c$ for **2**, $P2_1/n$ for **4**) with two pairs of enantiomers in the unit cell ($Z = 4$). The molecular structures are presented in Figures 2 and 3. Owing to the unsymmetrical substitution pattern, the cyclopropane rings have three different C–C bond lengths in both molecules [**2**: 1.554(5), 1.530(5), and 1.512(5) Å; **4**: 1.546(7), 1.495(7), and 1.508(7) Å]. Compared with the bond lengths of the unsubstituted cyclopropane [1.501(2) Å], all the C–C bonds of **2** and of **4** are slightly lengthened, probably as a consequence of both inductive and steric effects.

Figure 2. Molecular structure of 2-[2,2-bis(diphenylphosphanyl)vinyl]-1,1-bis(diphenylphosphanyl)cyclopropane (**2**) in the crystal. – Selected bond lengths [Å] and angles [°]: C1–C2 1.359(5), C2–C3 1.462(5), C3–C4 1.530(5), C3–C5 1.512(5), C4–C5 1.554(5), P1–C1 1.848(4), P2–C1 1.833(4), P3–C4 1.844(3), P4–C4 1.849(4); C3–C2–C1 126.1(3), C4–C3–C2 122.7(3), C5–C3–C2 118.9(3), C5–C3–C4 61.5(2), C5–C4–C3 58.7(2), C4–C5–C3 59.8(2), P2–C1–P1 118.7(2), C2–C1–P1 121.5(3), C2–C1–P2 119.8(3), P4–C4–P3 117.1(2), C3–C4–P3 120.0(3), C3–C4–P4 118.6(2), C5–C4–P3 117.3(3), C5–C4–P4 110.9(2)

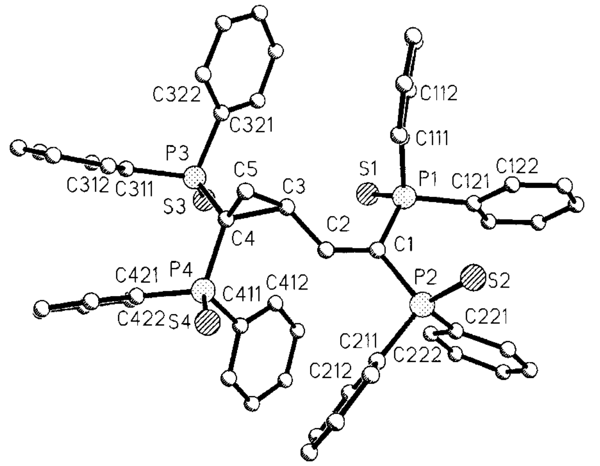


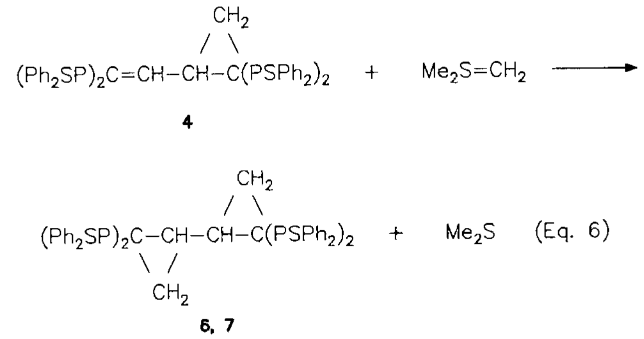
The C–C bond lengths of the vinyl parts are comparable to those in **1**. The P–C–P angles of **2** and **4** show no major deviations from standard values as in **1** or in 1,1-bis(diphenylphosphanyl)cyclopropane [118.0(2)°][7]. The sum of the angles at C1 is very close to 360° for **2** and **4** indicating a regular trigonal-planar configuration in both cases.

### Cyclopropanation of 2-[2,2-Bis(diphenylthiophosphinyl)-vinyl]-1,1-bis(diphenylthiophosphinyl)cyclopropane (4)

In contrast to the observations with the parent diphenylphosphanyl compound **1** and the monocyclopropanated derivative **2**, compound **4** readily undergoes a second cyclopropanation reaction. Concerning the chirality of **4**, the second cyclopropanation leads to an additional centre of asymmetry at C1 of vinyl, and hence to three stereoisomers. Both the 1*R*,1′*R*/1*S*,1′*S* enantiomers **6** and the achiral *meso*-bicyclopropyl compound **7** are formed as a mixture in good overall yield under mild conditions. The $^{31}P\{^1H\}$-NMR spectrum shows two doublet resonances with chemical shifts of $\delta = 39.32$ and 49.09 with a $J$(PP) value of 30.5 Hz, and two doublets at $\delta = 49.59$ and 52.01 with $J$(PP) = 13.1 Hz for the two diastereomers. No assignment of the individual resonances to **6** or **7** has been attempted. Integration of the signals exhibits a 1:1 ratio for **6** and **7**. Thus, the reaction is not diastereoselective. Compound **7** can be separated from the mixture by crystallization from dichloromethane/pentane. The crystals are colorless (m.p. 325°C), stable to air and moisture and soluble in tetrahydrofuran, $CH_2Cl_2$, $CHCl_3$, benzene, and toluene. Characterization by analytical and spectroscopic data is straightforward (see experimental section).

Figure 3. Molecular structure of 2-[2,2-bis(diphenylthiophosphinyl)vinyl]-1,1-bis(diphenylthiophosphinyl)cyclopropane (**4**) in the crystal. – Selected bond lengths [Å] and angles [°]: C1–C2 1.329(7), C2–C3 1.472(6), C3–C4 1.546(7), C3–C5 1.495(7), C4–C5 1.508(7), P1–C1 1.830(5), P2–C1 1.833(4), P3–C4 1.843(5), P4–C4 1.853(5), P1–S1 1.949(2), P2–S2 1.948(2), P3–S3 1.905(2), P4–S4 1.952(2); C3–C2–C1 128.3(5), C4–C3–C2 122.7(4), C5–C3–C2 118.4(4), C5–C3–C4 59.4(3), C5–C4–C3 58.6(3), C4–C5–C3 62.0(3), P2–C1–P1 121.3(3), C2–C1–P1 120.4(3), C2–C1–P2 118.0(4), P4–C4–P3 117.7(3), C3–C4–P3 115.7(3), C3–C4–P4 117.7(3), C5–C4–P3 117.2(3), C5–C4–P4 116.7(3)





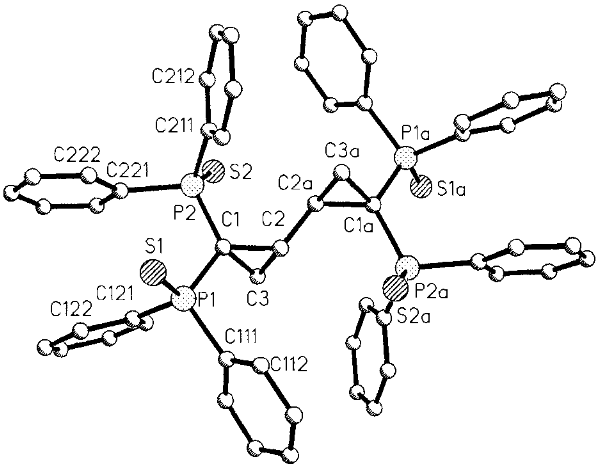
$$\underset{\mathbf{4}}{\mathrm{(Ph_2SP)_2C{=}CH{-}\overset{CH_2}{\overset{/\ \backslash}{CH{-}CH}}{-}C(PSPh_2)_2}} + \mathrm{Me_2S{=}CH_2} \longrightarrow$$

$$\underset{\mathbf{6,\ 7}}{\mathrm{\underset{\underset{CH_2}{\backslash\ /}}{(Ph_2SP)_2C{-}CH}{-}\overset{CH_2}{\overset{/\ \backslash}{CH{-}C(PSPh_2)_2}}}} + \mathrm{Me_2S} \quad \text{(Eq. 6)}$$

### Crystal and Molecular Structure of *meso*-2,2,2′,2′-Tetrakis(diphenylthiophosphinyl)-1,1′-bicyclopropyl (7)

The bicyclopropyl **7** crystallizes in monoclinic crystals (space group $P2_1/n$) with two molecules in the unit cell. The structure exhibits an *E* configuration with an inversion centre between the cyclopropyl carbon atoms C1 and C1′ (crystallographic numbering: C2, C2a, Figure 4). The second cyclopropanation remarkably affects the C–C bond lengths of the cyclopropane rings. Compared with the cyclopropane unit in **4**, the long bond in the former [C3–C4 = 1.546(7) Å] has turned into the shortest [C1–C2 = 1.45(1) Å], whilst the other two bonds have lengthened [C1–C3 = 1.64(2), C2–C3 = 1.58(2) Å]. Comparison with the structure of 1,1,4,4-tetrakis(diphenylthiophosphinyl)-1,3-butadiene[6] shows that the stepwise cyclopropanation has no influence on the length of the central C–C bond [butadiene[6]: C2–C2′ = 1.469(5), **4**: C2–C3 = 1.472(6), **7**: C1–C1′ = 1.45(1) Å]. The P–C–P angle [119.9(5)°] is intermediate between the P–C–P angles of **4** [117.7(3) and 122.6(2)°].

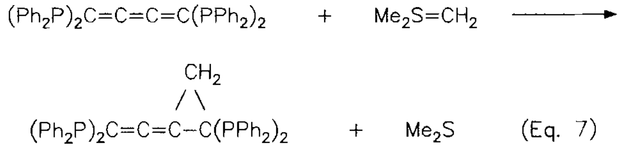
Figure 4. Molecular structure of *meso*-2,2,2′,2′-tetrakis(diphenylthiophosphinyl)-1,1′-bicyclopropyl (**7**) in the crystal. – Selected bond lengths [Å] and angles [°]: C1–C2 1.45(1), C1–C3 1.64(2), C3–C2 1.58(2), C2–C2a 1.45(1), P1–C1 1.815(7), P2–C1, 1.848(8), P1–S1 1.942(3), P2–S2 1.947(3); C1–C2a–C2 125.1(1), C3–C1–C2 60.9(8), C3–C2–C1 65.6(9), C2–C3–C1 53.5(8), P2–C1–P1 119.9(5)



## Synthesis, Properties, and Derivatives of the Vinylidenecyclopropane 8

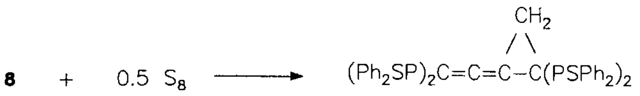
Under conditions similar to those employed for the preparation of the vinylcyclopropane from the parent butadiene **1**, tetrakis(diphenylphosphanyl)butatriene[13] reacts with dimethylsulfonium methylide to give 2-[2,2-bis(diphenylphosphanyl)vinylidene]-1,1-bis(diphenylphosphanyl)cyclopropane (**8**) (Eq. 7). Irrespective of variations in the experimental conditions or the presence of a deficit or an excess of dimethylsulfonium methylide, only one of the peripheral double bonds (1,2-position) has been found to react. Compound **8** was isolated as a white powder, m.p. 203°C, soluble in THF, $CH_2Cl_2$, $CHCl_3$, benzene, and toluene. It is stable to air and moisture.

The vinylidenecyclopropane **8** was converted into its tetrasulfide **9** by treatment with elemental sulfur in dichloromethane (Eq. 8). The derivative **9** is again a colorless crystalline solid, soluble in polar organic solvents and stable to air and moisture. Analytical and spectroscopic data of compound **8** and **9** are summarized in the experimental section.



$$(Ph_2P)_2C{=}C{=}C{=}C(PPh_2)_2 + Me_2S{=}CH_2 \longrightarrow (Ph_2P)_2C{=}C{=}\overset{CH_2}{\overset{/\backslash}{C{-}C}}(PPh_2)_2 + Me_2S \quad \text{(Eq. 7)}$$

**8**



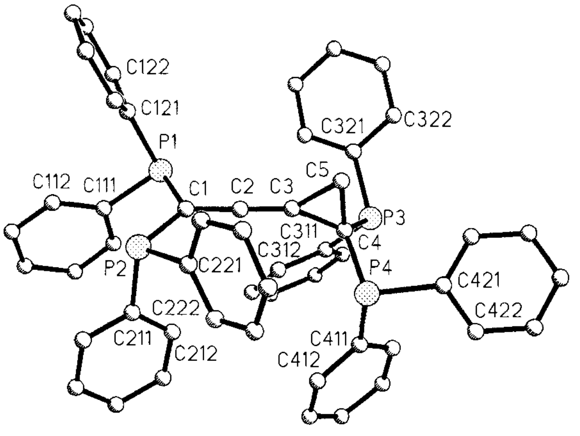
$$\mathbf{8} + 0.5\,S_8 \longrightarrow (Ph_2SP)_2C{=}C{=}\overset{CH_2}{\overset{/\backslash}{C{-}C}}(PSPh_2)_2$$

**9** (Eq. 8)

## Crystal and Molecular Structure of the Vinylidenecyclopropane 8

Compound **8** crystallizes from dichloromethane as colorless, monoclinic crystals (space group $P2_1/c$) with four molecules in the unit cell. The molecular structure is shown in Figure 5. The C=C bonds of the vinylidene unit show a long/short sequence with C1–C2 = 1.322(5) and C2–C3 = 1.267(4) Å. These values are very close to those in the parent tetrakis(diphenylphosphanyl)butatriene[13] [C1–C2 = 1.321(4), C2–C3 = 1.262(4), C3–C4 = 1.323(4) Å] or other standard butatrienes[17]. The bond lengths of the attached cyclopropyl group, however, are remarkably different from those of unsubstituted cyclopropane. The two vinylidene-adjacent bonds are shortened [C3–C5 = 1.470(5), C3–C4 = 1.487(5) Å] while the third one is longated [C4–C5 = 1.558(5) Å]. This result agrees with the picture of a cyclopropyl group resembling an ethylene unit, which in the present case is part of the cumulene system. The C=C=C angle at C2 is very close to 180°, indicating a cumulene bonding. The sum of the angles at C1 is 360° corresponding to a trigonal-planar configuration. The angle

Figure 5. Molecular structure of 2-[2,2-bis(diphenylphosphanyl)vinylidene]-1,1-bis(diphenylphosphanyl)cyclopropane (**8**) in the crystal. – Selected bond lengths [Å] and angles [°]: C1–C2 1.322(5), C2–C3 1.267(5), C3–C4 1.487(5), C3–C5 1.470(5), C4–C5 1.558(5), P1–C1 1.839(3), P2–C1 1.848(4), P3–C4 1.854(4), P4–C4 1.854(4); C3–C2–C1 179.0(4), C2–C3–C4 149.9(3), C2–C3–C5 146.5(3), C5–C3–C4 63.5(2), C3–C4–C5 57.7(2), C3–C5–C4 58.7(2), P1–C1–P2 122.6(2), C2–C1–P1 115.3(3), C2–C1–P2 122.1(3), P3–C4–P4 119.0(2), C3–C4–P3 122.9(3), C3–C4–P4 113.9(2), C5–C4–P3 118.0(3), C5–C4–P4 109.6(3)



C2−C3−C5 = 146.5(3)° is smaller as compared to its intramolecular counterpart C2−C3−C4 = 149.9(3)°, probably as a consequence of steric repulsion. Whilst the angle P3−C4−P4 = 119.0(2)° is normal, P1−C1−P2 = 122.6(2)° is slightly expanded.

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## Experimental

The experiments were 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. − MS: Varian MAT 311A.

*1,1,4,4-Tetrakis(diphenylphosphanyl)-1,3-butadiene* (**1**): A solution of 1,4-bis(diphenylphosphanyl)butadiyne (6.7 g, 16 mmol) in 150 ml of toluene is first mixed with the catalytic amount of 0.15 g of potassium *tert*-butoxide (1.3 mmol), followed by 5.59 g of diphenylphosphane (5.53 ml, 32 mmol). The reaction mixture is heated for 24 h at 70°C. After cooling to ambient temp. the precipitated yellow solid is collected, washed with toluene (50 ml) and hexane (50 ml), dried in vacuo, and crystallized from dichloromethane; yellow crystals (12.4 g, 98%). For analytical and spectroscopic data see ref.[6].

*2-[2,2-Bis(diphenylphosphanyl)vinyl]-1,1-bis(diphenylphosphanyl)cyclopropane* (**2**): A slurry of trimethylsulfonium iodide (6.53 g; 32 mmol) in tetrahydrofuran (50 ml) is treated at 0°C with a solution of *n*-butyllithium in hexane (19.3 ml; 1.66 M) during a period of 10 min with stirring. After another 10 min of vigorous agitation a solution of **1** (12.2 g; 15.44 mmol) in THF (75 ml) is added dropwise, and stirring is continued at 0°C for 30 min, at 20°C for 90 min, and finally at reflux temp. 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 oil is stirred with methanol, the precipitated white solid collected, washed with methanol (50 ml) and hexane (50 ml), dried in vacuo, and crystallized from dichloromethane; colorless crystals (9.56 g, 77%), m.p. 223°C. − $^{1}$H NMR (CDCl$_3$): δ = 0.81−0.93 (m, 1H, CH), 1.08−1.20 (m, 2H, *c*CH), 2.54−2.59 (m, 1H, =CH), 6.80−7.49 (m, 40H, Ph). − $^{31}$P NMR (CDCl$_3$): δ = −12.32 (s), −5.68 (s), −1.82 (s), 6.99 (s). − $^{13}$C NMR (CDCl$_3$): δ = 19.5 [dddd, $^{1}J$(PC) = 25.3 and 62.8, $^{4}J$(PC) = 1.6 and 1.1 Hz, *c*CP$_2$], 21.86 [d, $^{2}J$(PC) = 14.9 Hz, CH$_2$], 27.06 [dd, $^{2}J$(PC) = 34.1 and 7.2 Hz, *c*CH], 127.41−136.58 (m, Ph), 137.49 [dd, $^{2}J$(PC) = 12.1 and 5.5 Hz, =CH], 154.89 [dd, $^{1}J$(PC) = 23.6 and 26.4 Hz; CP$_2$]. − MS (EI, 70 eV), *m/z* (%): 804 (3.7) [M$^+$]; 619 (2.1) [M$^+$ − PPh$_2$]. − C$_{53}$H$_{44}$P$_4$ (804.8): calcd. C 79.10, H 5.51, P 15.39; found C 77.84, H 5.53, P 16.63.

*2-[2,2-Bis(diphenylphosphinyl)vinyl]-1,1-bis(diphenylphosphinyl)cyclopropane* (**3**): A solution of **2** (0.40 g; 0.5 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. Colorless crystals remain (0.39 g; 90%), m.p. 267°C. − $^{1}$H NMR (CDCl$_3$): δ = 0.8 [t, $^{3}J$(HH) = 7 Hz, 1H, *c*CH], 1.18−1.23 (m, 1H, *c*CH$_2$), 1.36−1.42 (m, 1H, *c*CH$_2$), 2.03−2.11 (m, 1H, =CH), 6.75−8.2 (m, 40H, Ph). − $^{31}$P NMR (CDCl$_3$): δ = 24.59 [d, $^{2}J$(PP) = 34.9 Hz], 29.35 [d, $^{2}J$(PP) = 34.9 Hz], 31.75 (s), 31.79 (s). − $^{13}$C NMR (CDCl$_3$): δ = 18.45 (m, CP$_2$), 25.5 (m, CH$_2$), 26.14 [t, $^{2}J$(PC) = 73 Hz, *c*CH], 127.0−133.4 (m, Ph), 134.8 (s, =CH), 161.1 (m, =CP$_2$). − C$_{53}$H$_{44}$P$_4$O$_4$ (868.8): calcd. C 73.27, H 5.10, O 7.37, P 14.26; found C 72.28, H 4.76, O 8.19, P 13.96.

*2-[2,2-Bis(diphenylthiophosphinyl)vinyl]-1,1-bis(diphenylthiophosphinyl)cyclopropane* (**4**): A solution of **2** (0.40 g; 0.5 mmol) in THF (10 ml) is treated with elemental sulfur (0.07 g; 2.19 mmol) at 20°C. After stirring for 30 min the solvent is removed in vacuo. The white solid is crystallized from dichloromethane/pentane; colorless crystals (0.37 g; 79%), m.p. 225°C. − $^{1}$H NMR (CDCl$_3$): δ = 0.88 [t, $^{3}J$(HH) = 6.8 Hz, 1H, *c*CH], 1.26−1.31 (m, 2H, *c*CH$_2$), 2.60−3.05 (m, 1H, =CH), 6.66−7.86 (m, 40H, Ph). − $^{31}$P NMR (CDCl$_3$): δ = 39.28 [d, $^{2}J$(PP) = 32.7 Hz], 49.09 [d, $^{2}J$(PP) = 32.7 Hz], 49.54 [d, $^{2}J$(PP) = 13.0 Hz], 51.99 [d, $^{2}J$(PP) = 13.0 Hz]. − $^{13}$C NMR (CDCl$_3$): δ = 20.75 (m, CP$_2$), 23.78 (m, CH$_2$), 27.7 (m, *c*CH), 125.8−136.8 (m, Ph), 156.0 (m, =CH), 158.35 (m, =CP$_2$). − MS (EI, 70 eV), *m/z* (%): 867 (2.6) [M$^+$ − 2 SH]. − C$_{53}$H$_{44}$P$_4$S$_4$ (933.1): calcd. C 68.22, H 4.75, S 13.74; found C 67.34, H 4.71, S 12.48.

*2-[2,2-Bis(diphenylselenophosphinyl)vinyl]-1,1-bis(diphenylselenophosphinyl)cyclopropane* (**5**): A solution of **2** (0.40 g; 0.5 mmol) in THF (10 ml) is treated with elemental grey selenium (0.166 g; 2.1 mmol) under reflux for 30 min. After cooling to ambient temp. the solvent is removed in vacuo. The remaining solid is crystallized from dichloromethane/pentane; colorless crystals (0.41 g, 73%), m.p. 203°C. − $^{1}$H NMR (CDCl$_3$): δ = 0.88 [t, $^{3}J$(HH) = 7 Hz, 1H, CH], 1.21 [d, $^{3}J$(HH) = 7.0 Hz, 2H, CH$_2$], 6.67 (m, 1H, =CH), 6.88−7.85 (m, 40H, Ph). − $^{31}$P NMR (CDCl$_3$): δ = 28.72 [d, $^{2}J$(PP) = 29 Hz], 42.89 (s), 43.06 [d, $^{2}J$(PP) = 29 Hz], 47.29 (s). − $^{13}$C NMR (CDCl$_3$): δ = 25.2−25.4 (m), 26.9−27.3 (m), 27.9−28.3 (m, *c*C), 125.4−137.0 (m, Ph and =CH), 154.6−154.85 (m, =CP$_2$). − C$_{53}$H$_{44}$P$_4$Se$_4$ (1120.7): calcd. C 56.80, H 3.96, Se 28.18; found C 57.32, H 4.21, Se 27.23.

*(1R,1R′)-/(1S,1S′)-/meso-2,2,2′,2′-Tetrakis(diphenylthiophosphinyl)-1,1′-bicyclopropyl* (**6**, **7**): A slurry of trimethylsulfonium iodide (8.3 mg, 0.04 mmol) in tetrahydrofuran (10 ml) is treated at 0°C with a solution of *n*-butyllithium in hexane (0.025 ml, 1.66 M) with stirring. After 10 min of vigorous agitation a solution of **4** (30 mg, 0.032 mmol) in THF (10 ml) is added dropwise, and stirring is continued at 0°C for 30 min, at 20°C for 90 min, and finally at reflux temp. for 2 h. After cooling to ambient temp. the solvents are removed in vacuo. The white solid is dissolved in 1 ml of dichloromethane and crystallized from dichloromethane/pentane; colorless crystals of **7** (11 mg, 30%), m.p. 325°C. − NMR data of the mixture of **6** and **7**: $^{1}$H NMR (CDCl$_3$): δ = 0.88−0.92 (m, 2H), 1.26−1.54 (m, 4H), 2.67−2.74 (m, 2H), 3.36−3.51 (m, 2H), 4.20−4.23 (m, 2H, CH), 6.71−7.84 (m, 80H, Ph). − $^{31}$P NMR (CDCl$_3$): δ = 39.22 [d, $^{2}J$(PP) = 30.5 Hz], 49.09 [d, $^{2}J$(PP) = 30.5 Hz], 49.59 [d, $^{2}J$(PP) = 13.1 Hz], 52.01 [d, $^{2}J$(PP) = 13.1 Hz]. − $^{13}$C NMR (CDCl$_3$): δ = 23.69 (s, CH$_2$), 23.97 (s, CH$_2$), 27.53 [t, $^{1}J$(CP) = 14.6 Hz, CP$_2$], 28.34 [t, $^{1}J$(PC) = 46.6 Hz, CP$_2$], 28.88 (s, CH), 30.32 (s, CH), 126.1−135.5 (m, Ph). − MS (EI, 70 eV), *m/z* (%): 946 (5) [M$^+$]. − C$_{54}$H$_{46}$P$_4$S$_4$ (947.1): calcd. C 68.48, H 4.89; found C 68.07, H 4.86.

*2-[2,2-Bis(diphenylphosphanyl)vinylidene]-1,1-bis(diphenylphosphanyl)cyclopropane* (**8**): A slurry of trimethylsulfonium iodide (5.5 g; 27 mmol) in tetrahydrofuran (150 ml) is treated at 0°C with a solution of *n*-butyllithium in hexane (16.3 ml; 1.66 M) during a period of 10 min with stirring. After another 10 min of vigorous agitation the reaction mixture is added to 10.6 g of 1,1,4,4-tetrakis(diphenylphosphanyl)butatriene (13.5 mmol). Stirring is continued at 0°C for 30 min, at 20°C for 90 min, and finally at reflux temp. for 2 h. After cooling to ambient temp., the solvents are removed in vacuo. The remaining viscous oil is stirred with ethanol, the resulting white solid is collected, washed with ethanol (50 ml) and hexane (50 ml), dried in vacuo, and crystallized from dichloromethane; colorless crystals (5.39 g, 49%), m.p. 203°C. − $^{1}$H NMR (CDCl$_3$): δ = 1.44 (m, 2H, CH$_2$), 7.02−7.35 (m, 40H, Ph). − $^{31}$P NMR (CDCl$_3$): δ = −5.94 (s), 6.92 (s). − $^{13}$C NMR (CDCl$_3$): δ =

22.11 [t, ${}^2J$(PC) = 9.2 Hz, $CH_2$], 24.44 [t, ${}^1J$(PC) = 50.6 Hz, $cCP_2$], 78.91 (m, $c$C=), 98.5 [t, ${}^1J$(PC) = 42.3 Hz, =$CP_2$], 126.7–137.1 (m, Ph), 201.7 [tt, ${}^2J$(PC) = 11.9, ${}^3J$(PC) = 2.8 Hz, =C=]. – MS (EI, 70 eV), *m/z* (%): 802 (3.3) [$M^+$], 617 (5.1) [$M^+ - PPh_2$]. – $C_{53}H_{42}P_4$ (802.8): calcd. C 79.29, H 5.27, P 15.43; found C 78.41, H 5.39, P 15.38.

*2-[2,2-Bis(diphenylthiophosphinyl)vinylidene]-1,1-bis(diphenylthiophosphinyl)cyclopropane* (**9**): A solution of **7** (0.40 g, 0.5 mmol) in THF (10 ml) is treated with elemental sulfur (0.07 g, 2.19 mmol) at 20°C for 30 min. Then the product is precipitated with ethanol (50 ml). After filtration the obtained white solid is washed with ether (30 ml) and hexane (30 ml), and dried in vacuo; white solid (0.39 g, 85%), m.p. 196°C. – ${}^1H$ NMR ($CDCl_3$): $\delta$ = 1.11–1.20 (m, 2H, $CH_2$), 6.6–8.2 (m, 40H, Ph). – ${}^{31}P$ NMR ($CDCl_3$): $\delta$ = 43.1 (s), 52.7 (s). – ${}^{13}C$ NMR ($CDCl_3$): $\delta$ = 15.23 (m, $CH_2$), 35.97 [tt, ${}^1J$(PC) = 36.8, ${}^4J$(PC) = 3.7 Hz, $CP_2$], 83.19 (m, $c$C=), 104.97 [t, ${}^1J$(PC) = 60.2 Hz, =$CP_2$], 127.17–134.11 (m, Ph), 204.82 [t, ${}^2J$(PC) = 3.7 Hz, =C=]. – MS (CI, positive ions), *m/z* (%): 867 (0.5) [$M^+ - 2$ S], 835 (0.9) [$M^+ - 3$ S], 803 (3) [$M^+ - 4$ S]. – $C_{53}H_{42}P_4S_4$ (931.05): calcd. C 68.37, H 4.55, P 13.31, S 13.77; found C 68.33, H 5.27, P 12.65, S 13.06.

*Crystal Structure Determinations:* Suitable crystals of compounds **1**, **2**, **4**, **7**, and **8** were mounted in glass capillaries and used for measurements of precise cell constants and intensity data

Table 1. Crystal data, data collection, structure solution and refinement for compounds **1**, **2**, **4**, **7**, and **8**

| | **1** | **2** | **4** | **7** | **8** |
|---|---|---|---|---|---|
| *Crystal data* | | | | | |
| Formula | $C_{52}H_{42}P_4$ | $C_{53}H_{44}P_4$ | $C_{53}H_{44}P_4S_4$ | $C_{56}H_{52}Cl_4OP_4S_4$ | $C_{53}H_{42}P_4$ |
| $M_r$ | 790.81 | 804.84 | 933.09 | 1135.00 | 802.75 |
| Crystal system | triclinic | monoclinic | monoclinic | monoclinic | monoclinic |
| Space group | $P\bar{1}$ [ No. 2] | $P2_1/c$ [No. 14] | $P2_1/n$ [No. 14] | $P2_1/n$ [No. 14] | $P2_1/c$ [No. 14] |
| a (Å) | 7.959(1) | 11.821(2) | 12.566(1) | 11.064(2) | 11.708(1) |
| b (Å) | 11.438(1) | 11.623(1) | 21.303(1) | 22.019(2) | 11.809(1) |
| c (Å] | 12.163(1) | 31.757(3) | 17.645(1) | 11.507(2) | 31.656(2) |
| $\alpha$ (°) | 90.86(1 | 90 | 90 | 90 | 90 |
| $\beta$ (°) | 95.54(1) | 95.64(1) | 96.66(1) | 108.33(1) | 98.97(1) |
| $\gamma$ (°) | 103.32(1) | 90 | 90 | 90 | 90 |
| V (Å$^3$) | 1071.6 | 4342.1 | 4691.4 | 2661.1 | 4323.0 |
| $\rho_{calc}$ (gcm$^{-3}$) | 1.220 | 1.231 | 1.320 | 1.410 | 1.233 |
| Z | 1 | 4 | 4 | 2 | 4 |
| F(000) (e) | 414 | 1688 | 1944 | 1176 | 1680 |
| $\mu$(Mo-K$_\alpha$) (cm$^{-1}$) | 2.05 | 2.04 | 3.63 | 5.31 | 2.10 |
| *Data collection* | | | | | |
| Diffractometer | | Enraf Nonius CAD4 | | | |
| Radiation | | Mo-K$_\alpha$ | | | |
| $\lambda$(Mo-K$_\alpha$) (Å) | | 0.71069, graphite monochromator | | | |
| T (°C) | +23 | -59 | +23 | -62 | +20 |
| Scan mode | $\omega$ | $\omega$ | $\theta$-$\theta$ | $\omega$ | $\omega$ |
| hkl range | ±9,±14,+14 | ±14,+14,+39 | ±14,+25,+20 | ±13,+26,+13 | +14,+14,±38 |
| sin($\theta$/$\lambda$)$_{max}$ (Å$^{-1}$) | 0.62 | 0.62 | 0.59 | 0.59 | 0.64 |
| Measured refl. | 4185 | 9304 | 8704 | 5048 | 9646 |
| Unique refl. | 3587 | 7559 | 6848 | 3944 | 8457 |
| Observed refl. | 2831 | 6042 | 4959 | 2769 | 8444 |
| $F_o \geq$ | 4$\sigma$($F_0$) | 4$\sigma$($F_0$) | 4$\sigma$($F_o$) | 4$\sigma$($F_o$) | 4$\sigma$($F_o$) |
| *Solution and Refinement* | | | | | |
| Refined parameters | 317 | 514 | 566 | 311 | 562 |
| Structure solution | direct methods | direct methods | direct methods | direct methods | direct methods |
| H atoms (found/calcd.) | 42/0 | 4/40 | 4/40 | 0/50 | 2/40 |
| R | 0.0413[a] | 0.0598[a] | 0.0515[a] | 0.0790[a] | 0.249[b] |
| $R_w$ | 0.0438[c] | 0.0584[c] | 0.0544[c] | 0.0870[c] | 0.096[a] |
| (shift/error)$_{max}$ | 0.000 | 0.002 | 0.000 | 0.000 | 0.000 |
| $\rho_{fin}$(max/min) (eÅ$^{-3}$) | +0.27/-0.17 | +0.83/-0.51 | +0.35/-0.77 | +1.13/-0.89[d] | +0.82/-0.43 |

[a] $R = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$. – [b] $R = [\Sigma w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]^{1/2}$. – $w = q/\sigma^2(F_o^2) + (ap)^2 + bp$. – $p = \max(f_o, 0) + 2F_c^2/3$. – $a = 0.1715$, $b = 0$. – [c] $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2]^{1/2}$. – $w = 1/\sigma^2(F_o)$. – [d] Residual electron densities located at the slightly disordered Cl atoms of the solvent molecules.

collection. Three standard reflections were measured periodically as a general check of crystal and instrument stability. No significant changes were observed for all five compounds. Diffraction intensities were corrected for Lp effects, whereas absorption corrections were not applied. All structures were solved and refined with the programs SHELXTL-PLUS (solution and refinement of **1**, **2**, **4**, and **7**) and SHELXTL-PLUS and SHELXL-93 (solution and refinement of **8**, respectively). The thermal motion of all non-hydrogen atoms was treated anisotropically, except for the O atom of the disordered water molecule in the crystal of **7**. Except for compound **1**, where all hydrogen atoms could be located, all phenyl hydrogen atoms were placed in calculated positions and allowed to ride on their corresponding carbon atoms. The cyclopropyl and/or ethylene H atoms were located and refined isotropically or included in the refinement with fixed isotropic contributions. The hydrogen atoms of the water molecule in **7** were neglected. Attempts to resolve the slight disorder of the $CH_2Cl_2$ molecule in **7** were not successful. Further information on crystal data, data collection, structure solution and refinement are summarized in Table 1. Selected interatomic distances and angles are listed in the corresponding figure captions. Tables of anisotropic thermal parameters, interatomic distances and angles as well as observed and calculated structure factors were deposited at the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen. The data are available on request on quoting the CSD number 58753.

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