251. Cyclopropylidenebis(diphenylphosphine): Note on its Synthesis, Properties and Spectral Data

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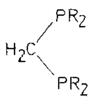
(21.IX.84)

Summary

The title compound has been synthesized through cyclopropanation of vinylidenebis(diphenylphosphine) using dimethylsulfoxonium methylide. It is easily converted into its dioxide and disulfide. NMR data of these first geminal diphosphinocyclopropanes are presented.

There is currently widespread interest in multifunctional tertiary phosphines with specific skeletal features which allow the induction of certain steric situations in the coordination sphere of metals. The construction of these ligands may be accomplished prior to the introduction into the metal complex, but alterations of the ligand may also become necessary while the phosphine is already coordinated. For these purposes the presence of functional groups or labile skeletal moieties is desirable. Topical examples are the CH-acidity of the CH_2-bridge in methylenebis(diphenylphosphine) (**1**, R = Ph; dpm) [1] [2] or the activated olefinic group of vinylidenebis(diphenylphosphine) (**2**, R = Ph) [3–5]. With the latter a variety of addition reactions can be carried out [5, 6]. We now report a facile synthesis of the title compound **3** (R = Ph) which contains an activated cyclopropane ring. This molecule is also of interest, since it is the first geminal bis(phosphino)cyclopropane, whose geometry must show subtle differences from the other two 1,3-difunctional bis(phosphines) **1** and **2**. Such small variations can be significant for dinuclear complexes with short metal-metal contacts [2] or, generally, for the 'bite' in mononuclear coordination compounds.

We have previously described work on the structure and complexes of phosphonium cyclopropylides **4**, which also can give access to cyclopropanes bearing more than one phosphorus substituents [6–11], and on some simple cyclopropylphosphines [12].



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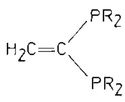

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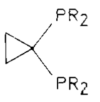

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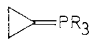

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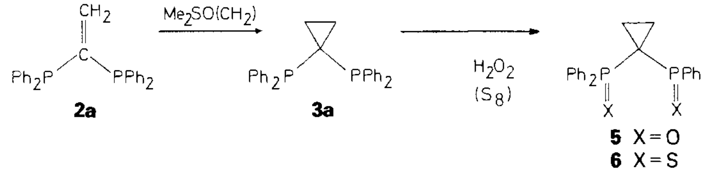
Results. – Out of the various methods for cyclopropanation the CH_2-transfer from dimethylsulfoxonium methylide $(CH_3)_2S(O)=CH_2$ [13–15] proved most satisfactory for a conversion of **2a** into **3a**. Yields in excess of 80% are obtained after 6 h in THF under reflux. The product **3a** forms colourless monoclinic needles (from EtOH), space group $C2/c$, $Z = 8$, $\rho_{calc.}$ 1.24 gcm^{-3}, with cell constants $a = 27.064(6)$, $b = 10.146(2)$, $c = 17.562(4)$ Å, $\beta = 114.30(2)°$ [16]. It is stable to air and moisture, m.p. 109 °C. NMR data are consistent with a molecule of C_{2v} or C_s symmetry in solution, indicating virtually free rotation of the PPh_2 groups around the P–C bonds. The symmetry is reduced in the conformation adopted in the crystal, similar to the observations with the olefin **2a** [4].



Compound **3a** is easily oxydized by H_2O_2 in aqueous THF to give the dioxide **5**, m.p. 206 °C. Cyclooctasulfur is added already at ambient temperature to yield the disulfide **6**, m.p. 201 °C. Like the parent diphosphine **3a**, these derivatives are powerful bidentate ligands for 'hard' or 'soft' metal centers, respectively. The NMR spectral data are summarized in the *Table*. They show no unusual features. The mass spectrum of the diphosphine **3a** was also found to confirm the composition of the molecule through the parent ion and a series of fragments consistent with the structural pattern. The coordination chemistry will be the subject of a forthcoming paper.

Table. *NMR Data of Compounds* **3a**, **5** *and* **6**[a])

	3a	**5**	**6**
$\delta(CH_2)(N), A_2A'_2XX'$	0.85 (14.8)	1.48 (23.8)	1.73 (25.0)
$\delta(C_6H_5), m$	7.0 to 7.6	7.0 to 8.0	7.0 to 8.1
$\delta(CH_2)(J), AX_2, t$	11.6 (6.3)	10.4 (< 1)	12.9 (< 1)
$\delta(CP_2)(J) AX_2, t$	8.2 (37.1)	15.2 (81.1)	15.6 (55.7)
$\delta(C(1))(N), AXX'$	136.6 (10.7)	130.5 (114.3)	130.0 (113.3)
$\delta(C(2))(N), AXX'$	133.6 (20.5)	132.0 (9.8)	132.7 (10.7)
$\delta(C(3))(N), AXX'$	127.7 (6.8)	127.9 (12.7)	127.3 (12.7)
$\delta(C(4)), s$	128.2	131.6	131.0
$\delta(P), s$	6.1	34.3	53.3

[a]) Spectra were recorded in $CDCl_3$ at 30°; δ-values are in ppm relative external TMS or H_3PO_4, J-values in Hz; N refers to the definition outlined in [3] [17]; ^{13}C- and ^{31}P-NMR spectra are ^1H-decoupled.

Experimental. – *Cyclopropylidenebis(diphenylphosphine)* (**3a**). A solution of 4.22 g (10.65 mmol) *vinylidenebis(diphenylphosphine)* (**2a**) [4] in 10 ml THF was treated with an excess of $Me_2S(O)CH_2$ in THF (16 mmol) [15], and the mixture heated with reflux for 6 h. After filtration from a fine precipitate the solvent was removed from the filtrate and the residue crystallized from EtOH/hexane [2,5:1]. Recrystallized material: yield 3.58 g (82%), m.p. 109°, colourless air-stable needles. MS (EI, 70 eV): 410 (71, M^+), 333 (24, M – Ph), 262

(100, Ph_3P), 185 (67, Ph_2P), 183 (97, $C_{12}H_8P$). Anal. calc. for $C_{27}H_{24}P_2$ (410.43): C 79.01, H 5.89; found C 78.03, H 5.82.

Cyclopropylidenebis(diphenylphosphine Oxide) (**5**). A solution of 0.79 g (1.92 mmol) **3a** in 10 ml THF was treated with 1 ml 30% aq. H_2O_2. After 30 min the solvent was removed *in vacuo* and the residue sublimed at 225°/10^{-3} Torr: 0.77 g (91%); colourless hygroscopic crystals, m.p. 206°. Anal. calc. for $C_{27}H_{24}O_2P_2$ (442.43): C 73.30, H 5.47, P 14.00; found: C 72.87, H 5.44, P 13.26.

Cyclopropylidenebis(diphenylphosphine sulfide) (**6**). A solution of 0.88 g (2.14 mmol) **3a** in 10 ml THF was stirred with 0.14 g sulfur (4.37 mmol) for 30 min at r.t. Excess sulfur was filtered and 30 ml EtOH added to the filtrate. The product crystallized from the hot solution on cooling: 0.9 g (88%), m.p. 201°, colourless airstable solid. Anal. calc. for $C_{27}H_{24}P_2S_2$ (474.55): C 68.34, H 5.10, found: C 67.63, H 5.43.

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