of P(O-*p*-tolyl)$_3$, 1.47 g (1.0 mmol) of Ni[P(O-*p*-tolyl)$_3$]$_4$, and 0.28 g (2.0 mmol) of ZnCl$_2$. Stirring was started, and the reaction temperature was adjusted to 68 °C. About 5 mL of HCN was placed in the bubbler and a nitrogen flow rate of 1.37 mL/h was started, which corresponded to 0.6 mmol of HCN/min. After 3 h, the HCN feed was stopped and the reaction mixture was cooled to room temperature. A GC analysis gave the following area percentages: ADN:MGN:ESN:T3PN:C3PN:4PN:T2PN:C2PN = 34.79:6.98:0.77:31.14:5.20:1.64:0.51:0.94. The conversion of PN's to DN's was approximately 52%, and the ratio of ADN/ADN + MGN + ESN was 0.815.

**$^1$H NMR Measurements of the Addition of HCN to (C$_2$H$_4$)Ni[P(O-*o*-tolyl)$_3$]$_2$.** In a typical experiment, 0.6 g (0.54 mmol) of Ni[P(O-*p*-tolyl)$_3$]$_3$ and 0.4 mL of toluene-*d*$_8$ were mixed in a 5-mm rubber-stoppered NMR tube. After the nickel catalyst was dissolved, the tube contents were cooled to −77 °C using a dry ice–acetone bath. Next, 8 mL (0.36 mmol) of ethylene gas was added to the tube with a gas-tight syringe, followed by 25 $\mu$L (1.2 mmol) of liquid HCN added by means of a chilled (0 °C) microliter syringe. $^1$H NMR spectra were then recorded as a function of time and temperature by using a Nicolet NT 360 WB spectrometer.

**Acknowledgment.** We are indebted to M. F. Wilson for running the experiment in which DCN was added to ethylene to show scrambling of deuterium between $\alpha$- and $\beta$-positions and to F. G. Kitson for GC/MS of the reaction products.

**Note Added in Proof.** The intermediate EtNiL$_2$CN [L = P(O-*o*-tolyl)$_3$] was shown to have a cis square-planar stereochemistry by the observation of a doublet ($J_{PC}$ = 35 Hz) for the *CH$_2$Ni at $\delta$ 11.6 in the $^{13}$C{$^1$H} spectrum generated from HCN and mono $^{13}$C-labeled (*C$_2$H$_4$)NiL$_2$ in toluene-*d*$_8$ at −50 °C. The doublet structure is attributed to coupling of the methylene carbon to the unique phosphorus trans to it; coupling to the cis-phosphorus is not observed. The methyl carbon at $\delta$ 14.1 shows no P–C coupling.

Identical $^{13}$C resonances are observed on adding *C$_2$H$_4$ to HNiL$_3$CN at −50 °C. Monotoring the product *C$_2$H$_5$CN (at $\delta$ 10.2) at −50 °C shows that its rate of formation *is the same* whether one adds HCN to (C$_2$H$_4$)NiL$_2$ or C$_2$H$_4$ to HNiL$_3$CN. This suggests that carbon–carbon coupling during the hydrocyanation of monoenes occurs in *cis*-RNiL$_2$CN, rather than in RNiL$_3$CN as shown in Figures 1–3.

**Registry No.** Ni[P(O-*o*-tolyl)$_3$]$_3$, 28829-00-7; Ni[P(O-*p*-tolyl)$_3$]$_3$, 87482-65-3; HNi[P(O-*o*-tolyl)$_3$]$_3$CN, 59220-71-2; (C$_2$H$_4$)Ni[P(O-*o*-tolyl)$_3$]$_2$, 31666-47-4; Ni[P(O-*o*-tolyl)$_3$]$_4$, 36841-11-9; EtNi[P(O-*o*-tolyl)$_3$]$_2$CN, 87482-66-4; HNi[P(O-*o*-tolyl)$_3$]$_3$CN·BPh$_3$, 87482-67-5; HNi[P(O-*o*-tolyl)$_3$]$_3$CN·B(*o*-tolyl)$_3$, 87482-68-6; PhNi(PPh$_3$)$_2$CN, 87482-69-7; AlCl$_3$, 7446-70-0; ZnCl$_2$, 7646-85-7; BPh$_3$, 960-71-4; B(*o*-tolyl)$_3$, 42270-57-5; BCy$_3$, 1088-01-3; B(OPh)$_3$, 1095-03-0; C$_2$F$_4$, 116-14-3; HCN, 74-90-8; C$_2$H$_4$, 74-85-1; (CH$_3$)$_3$CCH$_2$CH$_2$CN, 15673-05-9; ADN, 111-69-3; MGN, 28906-50-5; 2PN, 13284-42-9; C3PN, 16545-78-1; T3PN, 16529-66-1; 4PN, 592-51-8; ESN, 17611-82-4; acrylonitrile, 107-13-1; propionitrile, 107-12-0; propylene, 115-07-1; *n*-butyronitrile, 109-74-0; isobutyronitrile, 78-82-0; *tert*-butylethylene, 558-37-2; styrene, 100-42-5; 3-phenylpropionitrile, 645-59-0; 2-phenylpropionitrile, 1823-91-2; butadiene, 106-99-0; 2-methyl-3-butenenitrile, 16529-56-9; 1,3-hexadiene, 592-48-3; 1,5-hexadiene, 592-42-7; heptenenitrile, 87482-64-2.

**Supplementary Material Available:** Data illustrating the calculation of the relative rate constants $k_i$ (Figure 4) from the relative substrate and product concentrations at steady state and at $t$ = 0, starting with pure 4PN (2 pages). Ordering information is given on any current masthead page.

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(58) The actual isomer ratios of the 3PN used were T3PN:C3PN:4PN:T2PN:C2PN = 0.92:0.04:0.03:0.002:0.008.

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# Synthesis and Structure of Triphenylphosphonium Bis(diphenylstibino)methylide: A Conformational Study

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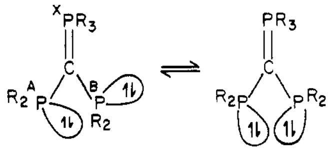
The title compound was prepared in a high-yield one-pot synthesis from chlorodiphenylstibine and triphenylphosphonium methylide. Methyltriphenylphosphonium chloride is the only transylidation by-product. The structure of the new ylide was determined by X-ray diffraction methods (monoclinic, space group $P2_1/n$, $Z = 4$, $a$ = 1094.7 (2) pm, $b$ = 1451.4 (2) pm, $c$ = 2276.8 (4) pm, $\beta$ = 90.67 (1)°). In the crystal, the molecule adopts the conformation B (R = C$_6$H$_5$) with the lone pairs of electrons at the antimony atoms oriented in the plane of the heavy atoms (P1, Sb1, Sb2) which also includes the ylidic carbon atom C1. The conformation is analogous to that found recently for the phosphorus compound A (R = C$_6$H$_5$) both in the crystal and in solution. The pronounced conformational preference is discussed in terms of lone pair repulsion and of electrostatic and steric forces. Parallels in the structures of diphosphinoamines and -methanides are pointed out, along with their relevance for coordination chemistry.

## Introduction

In a study of the structure and bonding in phosphino-substituted ylides A,[1] an important class of powerful ligands,[1-5] a striking preference for a rotational orientation of the lone pairs at the trivalent phosphorus atoms ($^A$P, $^B$P) was detected recently. Conformation A was found to prevail in solution, as shown by variable-temperature $^{31}$P nuclear magnetic resonance spectroscopy. For R = C$_6$H$_5$



A A′

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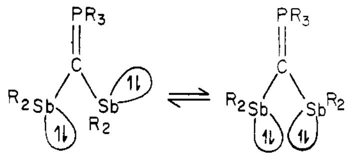
the two $P^{III}$ centers are nonequivalent even at room temperature in toluene solution and rotational barriers for the $P^{III}$–$C_{ylide}$ *single* bonds amount to as much as 10 ± 1 kcal $mol^{-1}$. Coupling constants for $^{X}P$–$^{A}P$ and $^{X}P$–$^{B}P$ differ considerably in sign and magnitude (173.4 and –42.7 Hz, respectively), as expected for an in-plane *E* or *Z* orientation of lone pairs of electrons at $P^{III}$ relative to the P=C—P skeleton.[1]

A single-crystal X-ray structure analysis of A (R = $C_6H_5$) has confirmed this configuration in the solid state. The $P_3C$ skeleton is planar, and the two lone pairs of electrons at phosphorus appear also to be in the heavy-atom plane, as extrapolated from the orientation of the phenyl groups. The symmetrical conformation A′ can be ruled out for both the solution and the solid state. Any chelating interaction with a metal center would thus require one C–$P^{III}$ rotation by 180° associated roughly with the energy barrier given above.[1]

The origin of the ground-state geometry A was assumed to be due to a minimization of the repulsive $^{A,B}P^{III}$ n pair/ylide π pair interaction and to a contribution from steric effects associated with the phenyl groups. In order to obtain experimental evidence as to the dependence of these conformational effects on the distance between the ylidic carbon atom and the group 5 element, the synthesis of the analogous diphenylantimony(III) derivative B was undertaken and its crystal structure determined. Antimony-substituted phosphorus ylides are still rare in the literature. A (dimethylstibino)methylphosphonium salt was obtained by Seyferth and Brändle in 1961.[6] The permethylated homologue B (R = $CH_3$) was synthesized in 1968, but structural details have not been elucidated.[7] B (R = $CH_3$) was also described as a cleavage product of transition-metal dimethylantimonide complexes with the salt-free ylide $(CH_3)_3P{=}CH_2$.[8] It should be pointed out that the antimony(III) functions in B have strongly enhanced donor properties as a consequence of the carbanionic character of the adjacent ylide carbon atom. Investigations with these ligands are in progress.



B B′

## Experimental Section

**Materials and Physical Measurements. Preparation of triphenylphosphonium bis(diphenylstibino)methylide B** was carried out under a dry, oxygen-free dinitrogen atmosphere. Toluene and pentane were dried and distilled over calcium hydride. Triphenylphosphonium methylide was prepared as described elsewhere.[9]

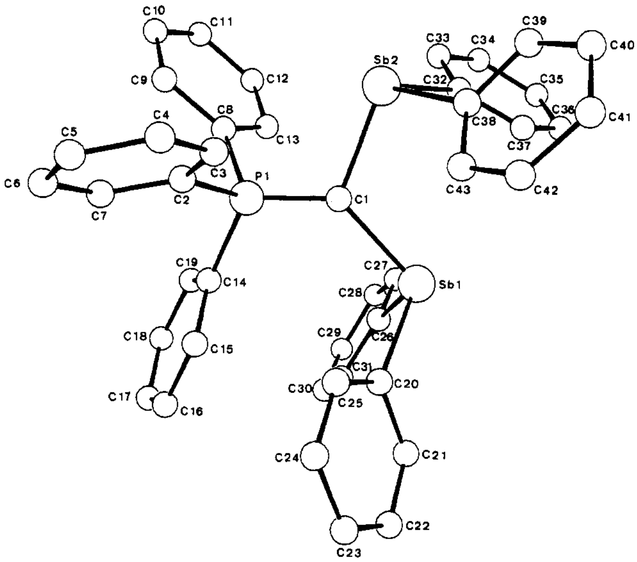


**Figure 1.** Perspective view of the molecule with the numbering of atoms. (Hydrogen atoms have been omitted for clarity.)

The IR spectrum of B was run on KBr disks with a Perkin-Elmer 577 and the $^{31}P$ NMR spectrum on a Bruker XL 90 (36.43 MHz) instrument. The melting point was determined in a sealed capillary by using a Büchi capillary melting point apparatus and is uncorrected.

**Preparation of Compounds.** Diphenylchlorostibine[10–13] was prepared in good yield according to the method of Bruker[10] by reduction of diphenylstibine trichloride hydrate $(C_6H_5)_2SbCl_3{\cdot}H_2O$ with disulfite or $SnCl_2$ in ethanolic hydrochloric acid (9%) solution. Diphenylchlorostibine separates as a light yellow oil, which crystallizes on cooling for several days at 5 °C. The solid was broken up, recrystallized from the same weight (!) of glacial acetic acid, and dried in vacuo over $P_2O_5$/KOH: colorless crystals; mp 70 °C (yield 80%).

**Diphenylstibine trichloride hydrate**[10] was obtained by reaction of phenylhydrazine hydrochloride with antimony trichloride in the presence of cupric chloride and atmospheric oxygen; mp 172–173 °C (yield 65%).

**Triphenylphosphonium Bis(diphenylstibino)methylide.** A solution of 3.02 g (9.7 mmol) of chlorodiphenylstibine in 20 mL of toluene was added dropwise to a vigorously stirred toluene solution of 4.03 g (14.46 mmol) of triphenylphosphonium methylide at 70 °C. Stirring is continued for 3 h. The yellowish white precipitate was separated from the yellow solution and washed several times with toluene (ca. 150 mL). The solvent was removed in vacuo, the yellow residue washed with 10 mL of toluene, followed by 10 mL of pentane, and dried in vacuo: mp 165 °C dec; yield 3.85 g (96% of theory); IR 975 (ν(P=C)), 510 (ν(Sb—C)) $cm^{-1}$; $^{31}P\{^1H\}$NMR (THF/$D_2O$, 85% $H_3PO_4$) δ 28.23. Anal. Calcd for $C_{43}H_{35}PSb_2$: C, 62.51; H, 4.27; Sb, 29.47. Found: C, 62.58; H, 4.34; Sb, 29.4.

**X-ray Data Collection and Structure Determination.** Single crystals of $C_{43}H_{35}PSb_2$ were obtained by crystallization from a toluene solution at 5 °C. A suitable crystal (0.15 × 0.2 × 0.18 mm) was mounted on a Nonius CAD 4 automatic four-circle diffractometer equipped with a graphite monochromator and a scintillation counter (ω–2θ scan mode, Mo Kα radiation, λ = 71.069 pm, *T* = 21 °C). The unit cell dimensions of *a* = 1094.7 (2) pm,

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Table I. Atomic Coordinates ($\times 10^4$) and Their Esd's and Thermal Parameters ($\times 10^3$) for $Ph_3P{=}C(SbPh_2)_2$

| atom | *x* | *y* | *z* | atom | *x* | *y* | *z* |
|---|---|---|---|---|---|---|---|
| Sb1 | 977 (1) | 1502 (1) | 1962 (1) | H3 | −959 | 4151 | 2215 |
| Sb2 | 1665 (1) | 3794 (1) | 2495 (1) | H4 | −2835 | 5104 | 2246 |
| P1 | 530 (1) | 3549 (1) | 1216 (1) | H5 | −3804 | 5599 | 1418 |
| C1 | 884 (4) | 2938 (3) | 1826 (2) | H6 | −2955 | 5474 | 526 |
| C2 | −834 (4) | 4275 (3) | 1282 (2) | H7 | −1063 | 4562 | 445 |
| C3 | −1353 (4) | 4406 (3) | 1832 (2) | H9 | 688 | 5452 | 898 |
| C4 | −2422 (4) | 4910 (3) | 1889 (2) | H10 | 2295 | 6447 | 539 |
| C5 | −2997 (4) | 5274 (3) | 1400 (2) | H11 | 4356 | 5835 | 522 |
| C6 | −2493 (5) | 5154 (4) | 855 (2) | H12 | 4762 | 4181 | 913 |
| C7 | −1422 (4) | 4657 (4) | 794 (2) | H13 | 3069 | 3274 | 1175 |
| C8 | 1761 (4) | 4329 (3) | 1010 (2) | H15 | −1559 | 2553 | 801 |
| C9 | 1601 (4) | 5257 (3) | 852 (2) | H16 | −1927 | 1553 | −96 |
| C10 | 2610 (5) | 5801 (4) | 717 (2) | H17 | −666 | 1575 | −827 |
| C11 | 3753 (5) | 5436 (4) | 724 (3) | H18 | 1342 | 2540 | −784 |
| C12 | 3932 (5) | 4529 (5) | 863 (3) | H19 | 1841 | 3212 | 56 |
| C13 | 2951 (4) | 3970 (3) | 1017 (2) | H21 | −98 | −350 | 1548 |
| C14 | 207 (4) | 2902 (3) | 545 (2) | H22 | −2147 | −1053 | 1399 |
| C15 | −917 (4) | 2454 (3) | 483 (2) | H23 | −4039 | −64 | 1314 |
| C16 | −1197 (5) | 1982 (4) | −29 (2) | H24 | −3745 | 1466 | 1691 |
| C17 | −384 (6) | 1975 (4) | −495 (2) | H25 | −1781 | 2135 | 1826 |
| C18 | 701 (5) | 2417 (4) | −438 (2) | H27 | 3497 | 1477 | 1545 |
| C19 | 1020 (4) | 2884 (4) | 85 (2) | H28 | 4820 | 965 | 664 |
| C20 | −817 (4) | 1003 (3) | 1709 (2) | H29 | 3955 | 431 | −199 |
| C21 | −937 (4) | 57 (3) | 1572 (2) | H30 | 1633 | 90 | −150 |
| C22 | −2069 (5) | −328 (4) | 1451 (2) | H31 | 330 | 646 | 638 |
| C23 | −3104 (5) | 198 (4) | 1476 (2) | H33 | 4481 | 3956 | 2103 |
| C24 | −3014 (4) | 1132 (4) | 1615 (2) | H34 | 6391 | 3428 | 2367 |
| C25 | −1884 (4) | 1506 (3) | 1740 (2) | H35 | 6433 | 1863 | 2864 |
| C26 | 1925 (4) | 1062 (3) | 1175 (2) | H36 | 4678 | 1109 | 3209 |
| C27 | 3188 (4) | 1193 (4) | 1176 (2) | H37 | 2697 | 2048 | 3169 |
| C28 | 3875 (5) | 957 (4) | 691 (3) | H39 | 1932 | 3854 | 3849 |
| C29 | 3324 (5) | 553 (4) | 209 (2) | H40 | 1051 | 3380 | 4691 |
| C30 | 2085 (5) | 414 (3) | 201 (2) | H41 | −1178 | 2645 | 4607 |
| C31 | 1377 (4) | 667 (3) | 685 (2) | H42 | −1973 | 2259 | 3697 |
| C32 | 3370 (4) | 3074 (3) | 2663 (2) | H43 | −882 | 2711 | 2782 |
| C33 | 4420 (5) | 3471 (4) | 2439 (2) | | | | |
| C34 | 5556 (5) | 3029 (4) | 2503 (3) | | | | |
| C35 | 5626 (5) | 2200 (4) | 2791 (2) | | | | |
| C36 | 4592 (5) | 1807 (4) | 3018 (2) | | | | |
| C37 | 3472 (4) | 2238 (4) | 2951 (2) | | | | |
| C38 | 704 (4) | 3247 (3) | 3247 (2) | | | | |
| C39 | 1167 (4) | 3441 (4) | 3806 (2) | | | | |
| C40 | 515 (5) | 3167 (4) | 4305 (2) | | | | |
| C41 | −592 (5) | 2732 (4) | 4250 (2) | | | | |
| C42 | −1069 (4) | 2559 (3) | 3683 (2) | | | | |
| C43 | −413 (4) | 2812 (3) | 3195 (2) | | | | |

| atom | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{12}$ | $U_{13}$ | $U_{23}$ |
|---|---|---|---|---|---|---|
| Sb1 | 49 | 36 | 34 | 1 | −2 | 1 |
| Sb2 | 50 | 40 | 38 | −1 | −8 | −5 |
| P1 | 37 | 34 | 29 | −1 | −3 | −1 |
| C1 | 48 | 31 | 33 | −1 | −6 | −3 |
| C2 | 41 | 35 | 39 | 3 | −2 | 0 |
| C3 | 48 | 49 | 39 | 1 | −1 | 1 |
| C4 | 50 | 54 | 55 | 5 | 8 | −4 |
| C5 | 43 | 50 | 80 | 11 | −2 | −3 |
| C6 | 58 | 6 | 69 | 17 | −17 | 14 |
| C7 | 59 | 63 | 44 | 12 | −2 | 8 |
| C8 | 46 | 42 | 31 | −5 | −3 | 1 |
| C9 | 63 | 44 | 44 | −6 | 0 | 0 |
| C10 | 79 | 52 | 62 | −16 | −8 | 12 |
| C11 | 74 | 76 | 77 | −33 | −5 | 23 |
| C12 | 45 | 93 | 96 | −12 | −3 | 19 |
| C13 | 46 | 56 | 67 | −3 | −4 | 10 |
| C14 | 46 | 35 | 31 | −1 | −3 | 0 |
| C15 | 56 | 50 | 42 | −4 | −7 | −2 |
| C16 | 69 | 50 | 65 | −8 | −24 | −7 |
| C17 | 95 | 61 | 50 | 9 | −22 | −17 |
| C18 | 86 | 87 | 47 | −4 | 15 | −23 |
| C19 | 57 | 65 | 42 | −7 | 9 | −11 |
| C20 | 50 | 46 | 27 | −4 | 8 | 1 |
| C21 | 63 | 50 | 44 | −12 | 7 | 0 |
| C22 | 83 | 51 | 63 | −24 | 15 | −5 |
| C23 | 67 | 95 | 48 | −33 | 3 | −7 |
| C24 | 47 | 87 | 53 | −5 | 4 | −5 |
| C25 | 61 | 48 | 42 | −5 | 5 | −5 |

Table I (*Continued*)

| atom | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{12}$ | $U_{13}$ | $U_{23}$ |
|---|---|---|---|---|---|---|
| C26 | 44 | 36 | 44 | 8 | 1 | 0 |
| C27 | 51 | 66 | 55 | −3 | −1 | −8 |
| C28 | 52 | 89 | 73 | 8 | 12 | 0 |
| C29 | 69 | 59 | 58 | 10 | 18 | 3 |
| C30 | 76 | 47 | 40 | 0 | 10 | −4 |
| C31 | 51 | 41 | 44 | 3 | 4 | −4 |
| C32 | 42 | 57 | 30 | −1 | −9 | −10 |
| C33 | 56 | 65 | 66 | −14 | 0 | 8 |
| C34 | 49 | 77 | 90 | −5 | 7 | 0 |
| C35 | 54 | 92 | 61 | 18 | −3 | −4 |
| C36 | 71 | 68 | 52 | 16 | −1 | 10 |
| C37 | 51 | 67 | 43 | 6 | 1 | 15 |
| C38 | 45 | 47 | 37 | 10 | −3 | −7 |
| C39 | 48 | 86 | 42 | 2 | 0 | −13 |
| C40 | 62 | 110 | 37 | 15 | 2 | −6 |
| C41 | 66 | 72 | 57 | 16 | 19 | 1 |
| C42 | 55 | 48 | 71 | 3 | 11 | −3 |
| C42 | 51 | 46 | 52 | 8 | −4 | −8 |

$b$ = 1451.4 (2) pm, $c$ = 2276.8 (4) pm, $\beta$ = 90.67 (1)°, and $V$ = 3617.33 × $10^6$ $pm^3$ were obtained by least squares from setting angles of 75 reflections ($4.35 \leq \theta \leq 17.75°$). Systematic absences indicated the monoclinic space group $P2_1/n$ ($Z = 4$, $D = 1.517$ g $cm^{-1}$). A total of 6754 reflections were collected ($\pm h,+k,+l$; $1.40 \leq \theta \leq 24.95°$): orientation (every 250 reflections) and intensity control (every 4000 s of X-ray exposure) by means of three standard reflections (062, $\bar{3}$, 1, 10, 517). Intensity data were corrected for Lorentz and polarization effects and for radiation damage; an absorption correction was not applied ($\mu$(Mo K$\alpha$) = 15.74 $cm^{-1}$). The reflections were merged to give 6328 unique reflections ($R_{int} = 0.017$) of which 1448 with $I \leq 2.0\sigma(I)$ were called unobserved. The structure was solved by the Patterson method (SHELX 76). All hydrogen atoms were located and included as fixed-atom contributions ($U_{iso} = 0.05$) in the refinement. Least-squares refinement of 415 parameters in five blocks converged at $R = \sum(\|F_o| - |F_c\|)/\sum|F_o| = 0.03$ for 4882 observed structure factors and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2} = 0.037$, where $w = 1/\sigma^2(F_o)$. A final difference Fourier syntheses revealed no anomalies in the unit cell (maximum residual $e$ density = 0.82 e/$Å^3$). The thermal parameter expression is defined as $U = \exp(-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*))$. The final positional and thermal parameters are listed in Table I and interatomic distances in Table II. Observed and calculated structure factors are available as supplementary material.

## Results

**Preparation and Characterization of the Title Compound $Ph_3P{=}C(SbPh_2)_2$ ($Ph = C_6H_5$).** There are various pathways for a synthesis of a stibino-substituted ylide of phosphorus, which differ in the number of steps required and the choice of starting materials.[14-16] It was desirable, however, to develop a one-pot procedure with the most readily available reagents; thus, attempts were made to combine all necessary derivatization and transylidation steps into one reaction sequence.

Optimum conditions were found in a 3:2 molar reaction of $Ph_3P{=}CH_2$ with $Ph_2SbCl$ in toluene as a solvent at 70 °C. After 3 h, the yield of $Ph_3P{=}C(SbPh_2)_2$ is greater than 95%, with $Ph_3PCH_3^+Cl^-$ as the sole byproduct. This phosphonium salt is the product of the transylidation steps where $Ph_3P{=}CH_2$ acts as a base to the stibino-substituted phosphonium salt intermediates. Separation of the final products presents no problem. The net reaction and the probable sequence of steps are described in Scheme I. There is precedent for such a reaction sequence in the chemistry of phosphino-, arsino-, and stibino-substituted ylides of phosphorus.[7,14] It is also generally accepted that organometalloid substituents enhance the CH acidity of onium salts.[17,18] This effect shifts the transylidation equilibria (2) and (4) to the right and, together with the relative lattice energy difference of the phosphonium salts involved, is responsible for the clear pattern of the overall reaction.

### Scheme I

$$Ph_3P{=}CH_2 + Ph_2SbCl \rightarrow Ph_3P^+{-}CH_2{-}SbPh_2Cl^- \quad (1)$$

$$Ph_3P^+{-}CH_2{-}SbPh_2Cl^- + Ph_3P{=}CH_2 \rightarrow Ph_3P{=}CH{-}SbPh_2 + Ph_3P^+CH_3Cl^- \quad (2)$$

$$Ph_3P{=}CH{-}SbPh_2 + Ph_2SbCl \rightarrow Ph_3P^+{-}CH(SbPh_2)_2Cl^- \quad (3)$$

$$Ph_3P^+{-}CH(SbPh_2)_2Cl^- + Ph_3P{=}CH_2 \rightarrow Ph_3P{=}C(SbPh_2)_2 + Ph_3P^+CH_3Cl^- \quad (4)$$

$$3Ph_3P{=}CH_2 + 2Ph_2SbCl \rightarrow Ph_3P{=}C(SbPh_2)_2 + 2Ph_3P^+CH_3Cl^- \quad (4)$$

$Ph_3P{=}C(SbPh_2)$ is a light yellow solid, mp 165 °C, which is surprisingly insensitive to air and moisture. It is only sparingly soluble in inert organic solvents, but a $^{31}P$ NMR singal can be obtained from solutions in hot tetrahydrofuran ($\delta$ 28.23, relative to $H_3PO_4$). The $\nu(P{=}C)$ stretching frequency is assigned at 975 $cm^{-1}$ in the IR spectrum of a KBr pellet of the microcrystalline material. The corresponding data for the phosphorus(III) homologue $Ph_3P{=}C(PPh_2)_2$ are $\delta$(P) 28.2 and $\nu(P{=}C)$ = 963 $cm^{-1}$ in A′.

**X-ray Crystallographic Studies and Description of the Structure.** Yellow single crystals of the title compound were obtained from saturated toluene solutions at 5 °C. Determination of the crystal and molecular structure of these crystals was straightforward following standard procedures (see Experimental Section). The results of the crystallographic study are summarized in Tables I and II and displayed in Figures 1 and 2.

The deviation of the ylidic carbon atom C1 from the plane of the heavy elements (P, Sb1, Sb2) is only 0.12 Å. Accordingly, the sum of the valence angles at C1 is 358.9 (2)°, with individual angles of 116.9 (2)° for Sb1–C1–Sb2 but of 130.5 (2) and 111.5 (2)° for P1–C1–Sb1 and P1–

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Table II. Bond Distances (Å) and Angles (deg) between Atoms and Selected Molecular Planes[a]

(a) Bond Distances

| | | | |
|---|---|---|---|
| P1-C1 | 1.692 (4) | Sb1-C1 | 2.110 (4) |
| P1-C2 | 1.835 (4) | Sb1-C20 | 2.165 (4) |
| P1-C8 | 1.825 (4) | Sb1-C26 | 2.176 (4) |
| P1-C14 | 1.825 (4) | Sb2-C1 | 2.136 (4) |
| C2-C3 | 1.393 (6) | Sb2-C32 | 2.170 (4) |
| C3-C4 | 1.388 (6) | Sb2-C38 | 2.172 (4) |
| C4-C5 | 1.380 (7) | C26-C27 | 1.396 (6) |
| C5-C6 | 1.376 (8) | C27-C28 | 1.386 (7) |
| C6-C7 | 1.385 (7) | C28-C29 | 1.379 (8) |
| C7-C2 | 1.393 (6) | C29-C30 | 1.371 (7) |
| C8-C9 | 1.406 (6) | C30-C31 | 1.404 (6) |
| C9-C10 | 1.396 (7) | C31-C26 | 1.386 (6) |
| C10-C11 | 1.359 (8) | C32-C33 | 1.389 (7) |
| C11-C12 | 1.368 (9) | C33-C34 | 1.406 (7) |
| C12-C13 | 1.395 (7) | C34-C35 | 1.372 (9) |
| C13-C8 | 1.403 (6) | C35-C36 | 1.374 (8) |
| C14-C15 | 1.398 (6) | C36-C37 | 1.383 (7) |
| C15-C16 | 1.384 (7) | C37-C32 | 1.384 (7) |
| C16-C17 | 1.392 (8) | C38-C39 | 1.394 (6) |
| C17-C18 | 1.355 (9) | C39-C40 | 1.406 (7) |
| C18-C19 | 1.411 (7) | C40-C41 | 1.372 (8) |
| C19-C14 | 1.383 (6) | C41-C42 | 1.411 (7) |
| C20-C21 | 1.414 (6) | C42-C43 | 1.379 (7) |
| C21-C22 | 1.385 (7) | C43-C38 | 1.381 (6) |
| C22-C23 | 1.368 (8) | | |
| C23-C24 | 1.396 (9) | | |
| C24-C25 | 1.378 (7) | | |
| C25-C20 | 1.380 (6) | | |

(b) Bond Angles

| | | | |
|---|---|---|---|
| P1-C1-Sb1 | 130.5 (2) | C1-P1-C2 | 114.4 (2) |
| P1-C1-Sb2 | 111.5 (2) | C1-P1-C8 | 111.9 (2) |
| Sb1-C1-Sb2 | 116.2 (2) | C1-P1-C14 | 117.3 (2) |
| C1-Sb1-C20 | 104.5 (2) | C2-P1-C8 | 105.7 (2) |
| C1-Sb1-C26 | 101.1 (2) | C2-P1-C14 | 102.4 (2) |
| C20-Sb1-C26 | 97.1 (1) | C8-P1-C14 | 103.9 (2) |
| C1-Sb2-C32 | 100.4 (2) | | |
| C1-Sb2-C38 | 99.0 (2) | | |
| C32-Sb2-C38 | 96.2 (2) | | |

(c) Molecular Planes

Plane 1: P1,Sb1,Sb2

$$10.1187x - 0.9894y - 8.7922z + 0.8842 = 0$$

Plane 2: Sb1,C20,C26

$$-2.1765x + 12.775y - 9.7594z + 0.2087 = 0$$

Plane 3: Sb2,C32,C38

$$3.4782x + 11.581y + 12.5514z - 7.9442 = 0$$

Deviation (Å) of Atoms from Plane 1: C1, −0.12; C2, −1.51; C8, +1.35; C14, +0.33; C20, −1.54; C26, +1.69; C32, +1.65; C38, −1.58

Angles between Planes:

| 1/2 | 94.71 | 1/3 | 88.11 | 2/3 | 68.01 |
|---|---|---|---|---|---|

[a] Esd's in units of the least significant figure in parentheses.

C1–Sb2, respectively. The large difference for the latter two angles is obviously due to the opposite orientation of the two $SbPh_2$ groups relative to the P1=C1 bond. It is this conformational orientation that is the most interesting feature of the molecular structure.

The average bond angle around C1 of 120° is indicative of coplanar $sp^2$ hybrid orbitals interacting with the pnicogen atoms in their common plane. The remaining $p_z$ orbital at C1 can thus be assumed to be engagred in $\pi$ bonding, in particular with the phosphonium center, and in fact, the distance P1=C1 of 1.692 (4) Å is evidence for at least partial multiple-bond character. This increased bond order for the ylidic function P1=C1 is also obvious from a comparison with the "internal reference" single bonds P1–C2, P1–C8, and P1–C14 which range from 1.825 (4) to 1.835 (4) Å.

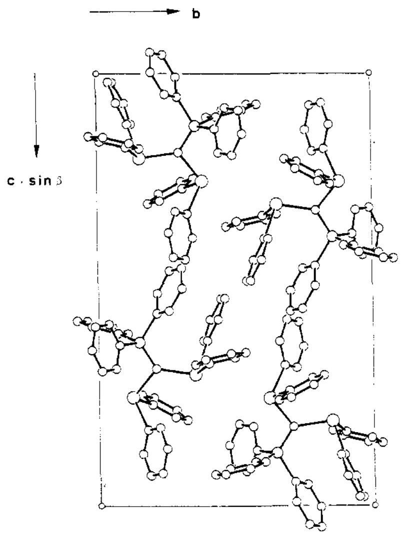


**Figure 2.** Contents of the unit cell viewed in projection along *a*.

There is much less difference between the distances Sb1–C1 and Sb2–C1 (2.110 (4) and 2.136 (4) Å) and the Sb–C(phenyl) bonds with values from 2.1650 (4) to 2.176 (4) Å. Thus the bonding between the ylidic carbon C1 and the antimony atoms, in contrast to the P1–C1 bond is to be taken as a normal Sb–C $\sigma$ single bond. The conformation in the crystal (and, for the P homologue, also in solution[1]) is therefore to be attributed to other forces, most likely the electrostatic and lone pair interaction of neighboring structural moieties. Intermolecular effects can be ruled out by the observation that no subnormal contacts or specific relative orientations of molecules are present in the structure (Figure 2).

**The Origin of the Ground State Conformation.** A calculation of the angles between some molecular planes (Table II) reveals that the two planes Sb1–C20–C26 and Sb2–C32–C38 are roughly perpendicular to the plane P1–Sb1–Sb2 (including C1, v.i.!), with angles of 94.71 and 88.11°, respectively. The lone pairs of electrons at Sb1 and Sb2, taken as $sp^3$ hybrids on the basis of the bond angles at Sb1/Sb2, thus have their main **p** vector in the heavy-atom plane of the molecule. It is in this orientation, however, that the Sb lone pairs have minimum (repulsive) overlap with the $p_z$ lone pair at carbon atom C1, which is oriented perpendicularly to the heavy-atom plane.

Also, in this array the steric interactions between the phenyl groups at adjacent $PPh_3$ and $SbPh_2$ or at adjacent $SbPh_2$ units are minimized, as is the repulsion between Sb lone pairs and phenyl groups of adjacent units. It can be easily seen from Figure 1 that the Sb1 lone pair is pointing toward a line bisecting the angle C32–Sb2–C38, while the same is true for the Sb2 lone pair and the bisector of C2–P1–C8 and finally the P1-bonded phenyl group C14–C19 relative to the bisector of C20–Sb1–C26. Relative phenyl plane orientation, on the other hand, seems to be more or less random or only partially dictated by interactions between adjacent $PPh_3/SbPh_2$ units.

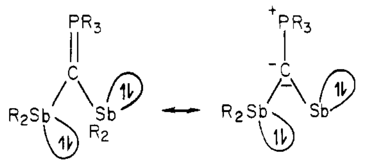
Another way of describing the conformation of the molecule is by the pertinent torsional angles presented in Table III, which again show the alternating orientation of phenyl groups above and below the heavy-atom plane. The torsional angle Sb1–C1–P1–C14 of −1.97° is numerical proof for the above assumption that the phenyl vector

Table III. Selected Torsional Angles (deg)

| | | | |
|---|---|---|---|
| Sb1-C1-P1-C2 | 117.96 | Sb2-C1-P1-C2 | -74.62 |
| Sb1-C1-P1-C8 | -121.93 | Sb2-C1-P1-C8 | 45.49 |
| Sb1-C1-P1-C14 | -1.97 | Sb2-C1-P1-C14 | 165.45 |
| C20-Sb1-C1-Sb2 | 135.38 | C32-Sb2-C1-Sb1 | 44.60 |
| C26-Sb1-C1-Sb2 | -123.24 | C38-Sb2-C1-Sb1 | -53.46 |

P1–C14–C17 is located in the PSb$_2$ plane.

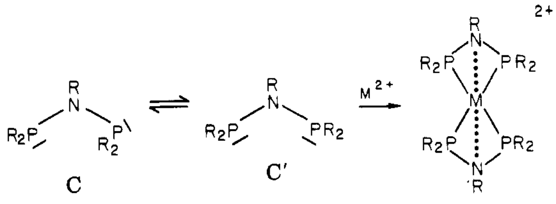
The bonding situation in phosphorus ylides is generally described by the two canonical formulas B and B″ as applied to the title compound. In the rotational ground state of the molecule detected in the crystal, the lone pair at Sb2 is therefore oriented toward the positively charged phosphonium center. If the Sb–C bonds are taken as polarized according to the traditional electronegativity tables as Sb$^{\delta+}$–C$^{\delta-}$, then the lone pair of electrons at Sb1 is clearly approaching the positively charged Sb2 atom. Both effects are giving rise to an electrostatic contribution to the total molecular energy. We consider these aspects as of minor importance, however, though the bond angles P1–C1–Sb2 = 111.5 (2)° and Sb1–C1–Sb2 = 116.4 (2)° (but P1–C1–Sb2 = 130.5 (2)°!) are in excellent agreement with the above description.



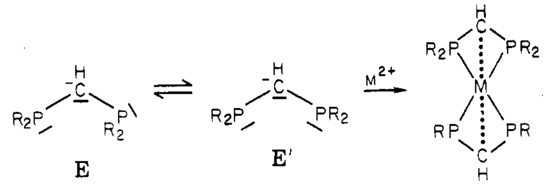
B B″

**Relevance for the Donor Properties in Metal Complexes.** Compounds A and B (and their arsenic analogues[7]) are potential chelating four- or even six-electron donor ligands, provided that the three donor sites (*P–C–P* or *Sb–C–Sb*, respectively) can be oriented toward the metal simultaneously. This orientation corresponds to the energy-rich conformation (A′) in the free donor ligands. However, this relation is certainly not valid for complexes formed where the metal–ligand interactions generate a new set of energy states.

A comparable situation was recently encountered with diphosphinoamines, which also have a conformation ground state as written in formula C but are attached to a metal in the configuration C′ as detected in complex D by X-ray diffraction studies.[19] For isoelectronic diphosphinomethanide anions E and E′ no structural information is available, but complexes derived therefrom are known to have structure F.[20–23]



C C′ D



E E′ F

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**Registry No.** Ph$_3$P=C(SbPh$_2$)$_2$, 87482-32-4; Ph$_2$SbCl$_3$, 21907-22-2; Ph$_3$P=CH$_2$, 19493-09-5.

**Supplementary Material Available:** A listing of calculated and observed structure factor amplitudes (20 pages). Ordering information is given on any current masthead page.

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