

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 ZnCl₂. 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.

¹H NMR Measurements of the Addition of HCN to (C₂H₄)Ni[P(O-*o*-tolyl)₃]₂. In a typical experiment, 0.6 g (0.54 mmol) of Ni[P(O-*o*-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 μL (1.2 mmol) of liquid HCN added by means of a chilled (0 °C) microliter syringe. ¹H 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 α- and β-positions and to F. G. Kitson for GC/MS of the reaction products.

Note Added in Proof. The intermediate EtNiL₂CN [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 *CH₂Ni at δ 11.6 in the ¹³C{¹H} spectrum generated from HCN and mono ¹³C-labeled (*C₂H₄)NiL₂

(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.

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 δ 14.1 shows no P-C coupling.

Identical ¹³C resonances are observed on adding *C₂H₄ to HNiL₃CN at -50 °C. Monitoring the product *C₂H₅CN (at δ 10.2) at -50 °C shows that its rate of formation is the same whether one adds HCN to (C₂H₄)NiL₂ or C₂H₄ to HNiL₃CN. This suggests that carbon-carbon coupling during the hydrocyanation of monoenes occurs in *cis*-RNiL₂CN, rather than in RNiL₃CN 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]₃CN, 59220-71-2; (C₂H₄)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]₂CN, 87482-66-4; HNi[P(O-*o*-tolyl)₃]₃CN-BPh₃, 87482-67-5; HNi[P(O-*o*-tolyl)₃]₃CN-B(*o*-tolyl)₃, 87482-68-6; PhNi(PPh₃)₂CN, 87482-69-7; AlCl₃, 7446-70-0; ZnCl₂, 7646-85-7; BPh₃, 960-71-4; B(*o*-tolyl)₃, 42270-57-5; BCy₃, 1088-01-3; B(OPh)₃, 1095-03-0; C₂F₄, 116-14-3; HCN, 74-90-8; C₂H₄, 74-85-1; (CH₃)₃CCH₂CH₂CN, 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-butenitrile, 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.

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

Hubert Schmidbaur,[†] Beatrix Milewski-Mahrla,[†] Gerhard Müller,^{†,‡} and Carl Krüger[‡]

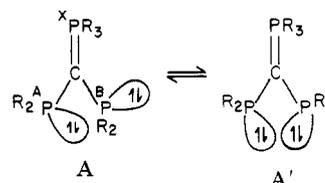
Anorganisch-chemisches Institut, Technische Universität München, D-8046 Garching, West Germany, and
Max-Planck-Institut für Kohlenforschung, D-4330 Mülheim, West Germany

Received July 19, 1983

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 *P*2₁/*n*, *Z* = 4, *a* = 1094.7 (2) pm, *b* = 1451.4 (2) pm, *c* = 2276.8 (4) pm, β = 90.67 (1)°). In the crystal, the molecule adopts the conformation B (R = C₆H₅) 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 = C₆H₅) 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 (^AP, ^BP) was detected recently. Conformation A was found to



prevail in solution, as shown by variable-temperature ³¹P nuclear magnetic resonance spectroscopy. For R = C₆H₅

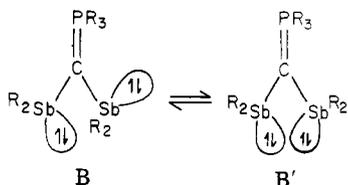
[†]Anorganisch-chemisches Institut.

[‡]Max-Planck-Institut für Kohlenforschung.

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 $^X P-AP$ and $^X P-BP$ 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. Anti-



mony-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.

Experimental Section

Materials and Physical Measurements. Preparation of triphenylphosphonium bis(diphenylstibino)methylide B was carried out under a dry, oxygen-free dinitrogen atmosphere.

- (1) Schmidbaur, H.; Deschler, U.; Milewski-Mahrla, B. *Chem. Ber.* 1983, 116, 1393. Schmidbaur, H.; Deschler, U. *Ibid.* 1983, 116, 1386.
- (2) Issleib, K.; Lindner, R. *Justus Liebigs Ann. Chem.* 1968, 713, 12; 1966, 699, 40. Issleib, K.; Abicht, H. P. *J. Prakt. Chem.* 1970, 312, 456.
- (3) Hussain, M. S.; Schmidbaur, H. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* 1976, 31B, 721. Schmidbaur, H.; Wohlleben-Hammer, A. *Chem. Ber.* 1979, 112, 510. Schmidbaur, H.; Deschler, U.; Milewski-Mahrla, B. *Angew. Chem.* 1981, 93, 598; *Angew. Chem., Int. Ed. Engl.* 1981, 20, 586.
- (4) Appel, R.; Wander, M.; Knoll, F. *Chem. Ber.* 1979, 112, 1093. Appel, R.; Erbeling, G. *Tetrahedron Lett.* 1978, 2689.
- (5) Karsch, H. H. *Chem. Ber.* 1982, 115, 1956. Karsch, H. H. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* 1979, 348, 1171.
- (6) Seyferth, D.; Brändle, K. A. *J. Am. Chem. Soc.* 1961, 83, 2055.
- (7) Schmidbaur, H.; Tronich, W. *Chem. Ber.* 1968, 101, 3545.
- (8) (a) Malisch, W.; Kuhn, M.; Albert, W.; Rössner, H. *Chem. Ber.* 1980, 113, 3318. (b) Malisch, W.; Panster, P. *J. Organomet. Chem.* 1974, 76, C7. (c) Luksza, M.; Fiederling, M.; Wanka, U.; Malisch, W. *J. Organomet. Chem.* 1982, 236, C1.

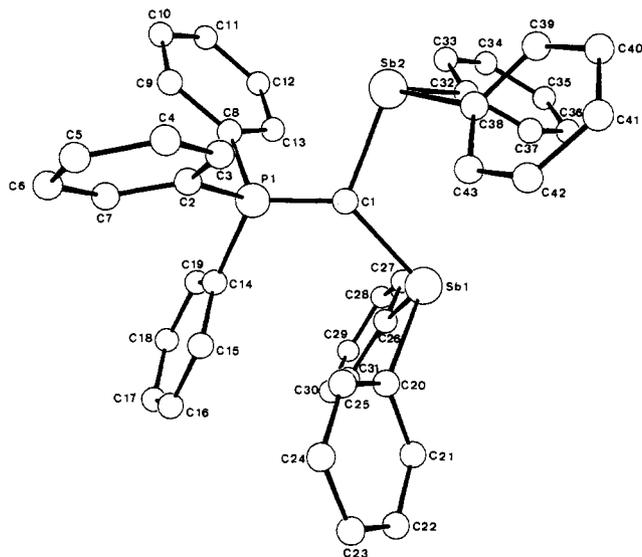


Figure 1. Perspective view of the molecule with the numbering of atoms. (Hydrogen atoms have been omitted for clarity.)

Toluene and pentane were dried and distilled over calcium hydride. Triphenylphosphonium methylide was prepared as described elsewhere.⁹

The IR spectrum of B was run on KBr disks with a Perkin-Elmer 577 and the ³¹P 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. Diphenylchlorostibine¹⁰⁻¹³ was prepared in good yield according to the method of Bruker¹⁰ 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 $5^\circ C$. 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 $70^\circ C$ (yield 80%).

Diphenylstibine trichloride hydrate¹⁰ was obtained by reaction of phenylhydrazine hydrochloride with antimony trichloride in the presence of cupric chloride and atmospheric oxygen; mp $172-173^\circ C$ (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 $70^\circ C$. 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 $165^\circ C$ dec; yield 3.85 g (96% of theory); IR 975 ($\nu(P=C)$), 510 ($\nu(Sb-C)$) cm^{-1} ; ³¹P{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 $5^\circ C$. A suitable crystal ($0.15 \times 0.2 \times 0.18$ mm) was mounted on a Nonius CAD 4 automatic four-circle diffractometer equipped with a graphite monochromator and a scintillation counter ($\omega-2\theta$ scan mode, Mo $K\alpha$ radiation, $\lambda = 71.069$ pm, $T = 21^\circ C$). The unit cell dimensions of $a = 1094.7$ (2) pm,

- (9) Schmidbaur, H.; Stühler, H.; Vornberger, W. *Chem. Ber.* 1972, 105, 1084.
- (10) Bruker, A. B. *Zh. Obsh. Khim.* 1961, 31, 974; *J. Gen. Chem. USSR (Engl. Transl.)* 1961, 31, 901.
- (11) Wieber, M. In "Gmelin Handbook of Inorganic Chemistry", 8th ed.; Springer-Verlag: Berlin, 1980-1982.
- (12) Issleib, K.; Hamann, B. *Z. Anorg. Allg. Chem.* 1966, 343, 196.
- (13) Blicke, F. F.; Oakdale, U. O.; Smith, F. D. *J. Am. Chem. Soc.* 1931, 53, 1025.

Table I. Atomic Coordinates ($\times 10^4$) and Their Esd's and Thermal Parameters ($\times 10^3$) for $\text{Ph}_3\text{P}=\text{C}(\text{SbPh}_2)_2$

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) $^\circ$, and $V = 3617.33 \times 10^6$ pm 3 were obtained by least squares from setting angles of 75 reflections ($4.35 \leq \theta \leq 17.75^\circ$). Systematic absences indicated the monoclinic space group $P2_1/n$ ($Z = 4$, $D = 1.517$ g cm $^{-3}$). A total of 6754 reflections were collected ($\pm h, +k, +l$; $1.40 \leq \theta \leq 24.95^\circ$): 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 ($\mu(\text{Mo K}\alpha) = 15.74$ cm $^{-1}$). The reflections were merged to give 6328 unique reflections ($R_{\text{int}} = 0.017$) 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 ($U_{\text{iso}} = 0.05$) 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.

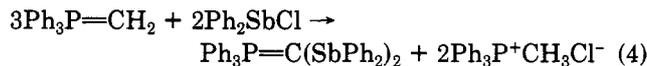
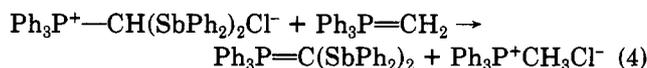
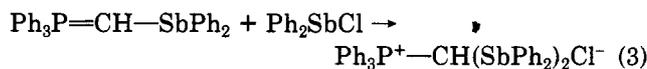
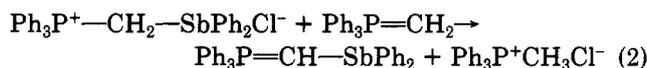
Results

Preparation and Characterization of the Title Compound $\text{Ph}_3\text{P}=\text{C}(\text{SbPh}_2)_2$ ($\text{Ph} = \text{C}_6\text{H}_5$). 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 $\text{Ph}_3\text{P}=\text{CH}_2$ with Ph_2SbCl in toluene as a solvent at 70 $^\circ\text{C}$. After 3 h, the yield of $\text{Ph}_3\text{P}=\text{C}(\text{SbPh}_2)_2$ is greater than 95%, with $\text{Ph}_3\text{PCH}_3^+\text{Cl}^-$ as the sole byproduct. This phosphonium salt is the product of the transylidation steps where $\text{Ph}_3\text{P}=\text{CH}_2$ 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



$\text{Ph}_3\text{P}=\text{C}(\text{SbPh}_2)_2$ is a light yellow solid, mp 165 $^\circ\text{C}$, which is surprisingly insensitive to air and moisture. It is only sparingly soluble in inert organic solvents, but a ^{31}P NMR signal can be obtained from solutions in hot tetrahydrofuran (δ 28.23, relative to H_3PO_4). The $\nu(\text{P}=\text{C})$ 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 $\text{Ph}_3\text{P}=\text{C}(\text{PPh}_2)_2$ are $\delta(\text{P})$ 28.2 and $\nu(\text{P}=\text{C}) = 963$ 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 $^\circ\text{C}$. 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) $^\circ$, with individual angles of 116.9 (2) $^\circ$ for Sb1-C1-Sb2 but of 130.5 (2) and 111.5 (2) $^\circ$ for P1-C1-Sb1 and P1-

(14) Schmidbaur, H. *Acc. Chem. Res.* 1975, 8, 62.

(15) Weber, L. "The Chemistry of the Metal-Carbon Bond"; Hartley, F. R., Patai, S., Ed.; Wiley: New York, 1982.

(16) Kaska, W. C. *Coord. Chem. Rev.* 1983, 48, 1.

(17) Peterson, D. J. *J. Organomet. Chem.* 1967, 8, 199.

(18) (a) Mathiason, D. R.; Miller, N. E. *Inorg. Chem.* 1968, 7, 709. (b) Miller, N. E. *Ibid.* 1965, 4, 1458.

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 SbPh₂ 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 sp² hybrid orbitals interacting with the pnictogen atoms in their common plane. The remaining p_z orbital at C1 can thus be assumed to be engaged in π 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

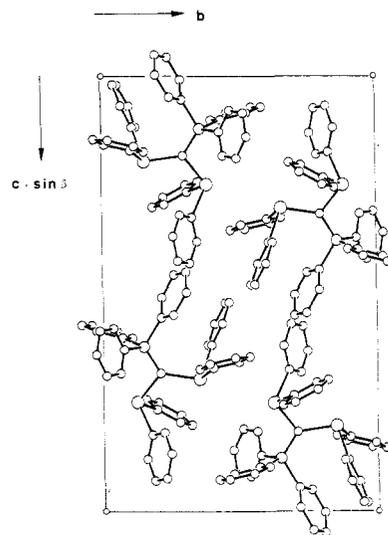


Figure 2. Contents of the unit cell viewed in projection along *a*.

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.

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 σ single bond. The conformation in the crystal (and, for the P homologue, also in solution¹) 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 sp³ 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 PPh₃ and SbPh₂ or at adjacent SbPh₂ 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 PPh₃/SbPh₂ units.

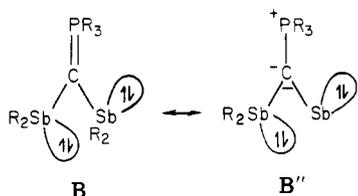
Another way of describing the conformation of the molecule is by the pertinent torsional angles presented in Table III, which again show the alternating orientation of phenyl groups above and below the heavy-atom plane. The torsional angle Sb1-C1-P1-C14 of -1.97° is numerical proof for the above assumption 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 PSb₂ 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

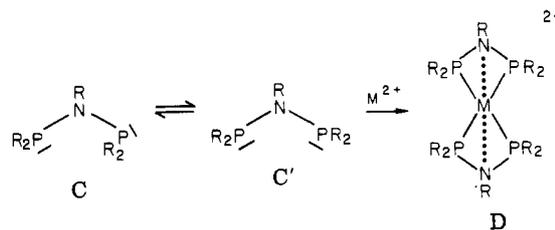


of the molecule detected in the crystal, the lone pair at Sb2 is therefore oriented toward the positively charged phosphonium center. If the Sb-C bonds are taken as polarized according to the traditional electronegativity tables as Sb^{δ+}-C^{δ-}, then the lone pair of electrons at Sb1 is clearly approaching 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.

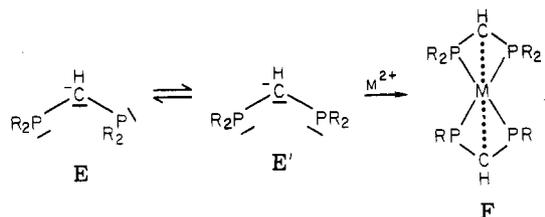
Relevance for the Donor Properties in Metal Complexes. Compounds A and B (and their arsenic analogues⁷) are potential chelating four- or even six-electron donor ligands, provided that the three donor sites (P-C-P or Sb-C-Sb, respectively) can be oriented toward the metal simultaneously. This orientation 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



Acknowledgment. This work was generously supported by Fonds der Chemischen Industrie, Frankfurt/Main, and Deutsche Forschungsgemeinschaft, Bonn-Bad Godesberg. We thank Professor M. Wieber, Universität Würzburg, for a sample of Ph₂SbCl.

Registry No. Ph₃P=C(SbPh₂)₂, 87482-32-4; Ph₂SbCl₃, 21907-22-2; Ph₃P=CH₂, 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.

(19) Schmidbaur, H.; Lautenschläger, S.; Milewski-Mahrla, B. *J. Organomet. Chem.* **1983**, *250*, 171.

(20) Shaw, B. L.; Al-Jibori, S. *J. Chem. Soc., Chem. Commun.* **1982**, 286.

(21) Browning, J.; Bushwell, G. W.; Dixon, K. R. *J. Organomet. Chem.* **1980**, *198*, C11.

(22) Brown, M. P.; Avari, A. Y. *J. Organomet. Chem.* **1982**, *236*, C33.

(23) Bassett, J. M.; Mandl, J. R.; Schmidbaur, H. *Chem. Ber.* **1980**, *113*, 1145.