CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF COLORADO, BOULDER, COLORADO 80302

The Lithium Tetraphosphinoaluminate Phosphination of Halosilanes and -germanes[1]

BY ARLAN D. NORMAN AND DALE C. WINGELETH

Received February 28, 1969

Lithium tetraphosphinoaluminate, $LiAl(PH_2)_4$, has been found to be a highly effective phosphinating agent for the preparation of phosphinosilanes and -germanes. Silylphosphine, $Si_2H_5PH_2$, and GeH_3PH_2 have been prepared in high yields from reactions of $LiAl(PH_2)_4$ with SiH_3Br, Si_2H_5Br, and GeH_3Br, respectively. Previously unreported vapor tension *vs.* temperature data for GeH_3PH_2 have been determined. The reactions of $LiAl(PH_2)_4$ with SiH_2Br_2 and $SiHBr_3$ result in formation of two new hydrides, $SiH_2(PH_2)_2$ and $SiH(PH_2)_3$. Bis(phosphino)silane and $SiH(PH_2)_3$ have been characterized on the basis of elemental analyses and ir, ^1H nmr, ^{31}P nmr, and mass spectral analyses. Reactions of nominally equimolar $LiAl(PH_2)_4$–$LiAlH_4$ mixtures with $GeCl_4$ and $SiCl_4$ result in coreduction and phosphination of the tetrahalides, the latter reaction providing a convenient synthesis of easily separated mixtures of SiH_3PH_2, $SiH_2(PH_2)_2$, and $SiH(PH_2)_3$.

Introduction

The importance of alkali metal hydroaluminates, *e.g.*, $LiAlH_4$, as efficient reducing agents is generally recognized. In marked contrast, the synthetic potential of analogous complex aluminates such as lithium tetraphosphinoaluminate, $LiAl(PH_2)_4$,[2] is poorly understood. Finholt, *et al.*, reported that $LiAl(PH_2)_4$ readily converted ethyl iodide to ethylphosphine; however, its usefulness as a general phosphinating agent was not examined. This fact, along with the desirability of finding an efficient method for the preparation of unsubstituted monophosphinosilanes and -germanes, *i.e.*, SiH_3PH_2 and GeH_3PH_2, and previously unreported multiply PH_2-substituted hydrides prompted us to examine $LiAl(PH_2)_4$ as a potential general phosphinating agent. The results of this investigation, which include the high-yield synthesis of SiH_3PH_2, GeH_3PH_2, and $Si_2H_5PH_2$ and the preparation and characterization of two new ternary hydrides, $SiH_2(PH_2)_2$ and $SiH(PH_2)_3$, are reported below.

Experimental Section

Apparatus.—All work was carried out in a standard high-vacuum system.[3,4] Vapor pressure *vs.* temperature data were collected using an all-glass immersible tensimeter (mercury manometer) which had been pretreated with a sample of the material for a period of 8–13 hr. Melting points were obtained by the Stock magnetic plunger technique. Mass spectra were obtained with a Consolidated Electrodynamics Corp. Model 21-103 spectrometer (ionizing voltage 70 eV). The inlet chamber of the spectrometer was predried with SiH_3PH_2 before each analysis in order to minimize sample hydrolysis. Infrared spectra were recorded with Perkin-Elmer Model 21 and Beckman IR-5 spectrometers, on gaseous samples in 10-cm cells fitted with NaCl and KBr windows. Proton nuclear magnetic resonance spectra were obtained at 60.0 and 100.0 MHz using Varian Associates A-60A and HA-100 spectrometers, respectively. Phosphorus-31 spectra were obtained at 40.5 MHz using the HA-100 spectrometer. Proton chemical shift values are reported relative to internal $(CH_3)_4Si$. Phosphorus-31 chemical shifts are given relative to 85% H_3PO_4.

Materials.—Phosphine,[5] SiH_3Br,[6] SiH_2Br_2,[7] $SiHBr_3$,[7] Si_2H_5Br,[7] and GeH_3Br[8] were prepared and purified using standard methods. Silicon tetrachloride (Afla Inorganics) and $GeCl_4$ (Germanium Research Institute) were purified by routine fractional condensation techniques. Lithium tetrahydroaluminate ($LiAlH_4$) was recrystallized from diethyl ether and stored under dry nitrogen. Diglyme (bis(2-methoxyethyl) ether) and triglyme (1,2-bis(2-methoxyethoxy)ethane) were distilled at reduced pressure from $LiAlH_4$ prior to use.

Preparation of $LiAl(PH_2)_4$ Solutions.—The $LiAl(PH_2)_4$ solutions were prepared from the reaction of PH_3 with $LiAlH_4$ in diglyme or triglyme (eq 1) during 72–96 hr as described previously by Finholt, *et al.*[2]

$$4PH_3 + LiAlH_4 \longrightarrow LiAl(PH_2)_4 + 4H_2 \qquad (1)$$

Based on the quantity of PH_3 consumed in each reaction, the per cent conversion of $LiAlH_4$ to $LiAl(PH_2)_4$ was calculated. One hundred per cent conversion was generally not achieved, because after a reaction period of more than 96 hr slight decomposition of the $LiAl(PH_2)_4$ solutions occurred. The solutions used in the cophosphination reduction reactions were prepared by allowing approximately 50% of the PH_3 required in eq 1 to react with $LiAlH_4$. For convenience these solutions are described as containing nominal quantities of $LiAl(PH_2)_4$ and $LiAlH_4$; however, it is recognized that the solutions likely consist of a complex mixture of $LiAlH_n(PH_2)_{4-n}$ species.

Syntheses of Phosphinosilanes and -germanes.—Reaction conditions for typical syntheses of the phosphinosilanes and -germanes are shown in Table I. In each case the halosilane or -germane was condensed into a 1-l. bulb containing solutions of $LiAl(PH_2)_4$ or $LiAl(PH_2)_4$–$LiAlH_4$ in 5–10 ml of diglyme or triglyme. Diglyme can be used satisfactorily in all syntheses except those of $SiH(PH_2)_3$, where the lower volatility triglyme is advantageous. In each case the reaction mixture was allowed to warm slowly to the indicated temperature. Reaction appears to begin somewhat below this temperature as evidenced by slight effervescence of the reaction mixtures as the mixtures melted. Upon completion of the reactions carried out in diglyme volatile materials (excepting the bulk solvent) were pumped into the vacuum line and passed through traps maintained at −23, −160, and −196°. The −196 and −23° traps condensed a SiH_4 (or GeH_4)-PH_3 mixture and the diglyme, respectively. With reactions carried out in triglyme, the −23° trap was replaced by a

---

[1] This work was supported by grants from the National Science Foundation (GP-8090) and the Petroleum Research Fund (941-G).

[2] A. E. Finholt, C. Helling, V. Imhof, L. Nelson, and E. Jacobsen, *Inorg. Chem.*, **2**, 504 (1963).

[3] A. Stock, "Hydrides of Boron and Silicon," Cornell University Press, Ithaca, N. Y., 1933.

[4] R. T. Sanderson, "High Vacuum Manipulation of Volatile Compounds," John Wiley & Sons, Inc., New York, N. Y., 1948.

[5] S. D. Gokhale and W. L. Jolly, *Inorg. Syn.*, **10**, 34 (1967).

[6] L. G. Ward, *ibid.*, **11**, 159 (1968).

[7] J. E. Drake and J. Simpson, *J. Inorg. Nucl. Chem. Letters*, **2**, 219 (1966).

[8] K. M. Mackay, P. Robinson, E. S. Spanier, and A. G. MacDiarmid, *J. Inorg. Nucl. Chem*, **28**, 1377 (1966).

TABLE I

SYNTHESES OF PHOSPHINOSILANES AND -GERMANES

Reactants (mmol)	Time, min (temp, °C), solvent	Products (mmol)
SiH_3Br (25.0) $LiAl(PH_2)_4$ (8.2)[a]	20 (−45), diglyme	SiH_4 (2.4)[c] PH_3 (3.1) $SiH_2(PH_2)_2$ (0.2) SiH_3PH_2 (20.4; 82% yield)
Si_2H_5Br (7.01) $LiAl(PH_2)_4$ (2.10)[a]	20 (−45), diglyme	SiH_4 (0.10)[c] PH_3 (0.77) Si_2H_6 (1.01) $Si_2H_5PH_2$ (4.40; 63% yield)
SiH_2Br_2 (4.03) $LiAl(PH_2)_4$ (2.84)[a]	10 (−30), diglyme	SiH_4 (0.24)[c] PH_3 (0.44) SiH_3PH_2 (0.68) $SiH_2(PH_2)_2$ (1.65; 41% yield)
$SiHBr_3$ (2.11) $LiAl(PH_2)_4$ (2.41)[a]	15 (−30), triglyme	SiH_4 (0.37)[c] PH_3 (0.78) SiH_3PH_2 (0.33) $SiH_2(PH_2)_2$ (0.42) $SiH(PH_2)_3$ (0.38; 18% yield)
$SiCl_4$ (25.4) $LiAl(PH_2)_4$ (14.1)[b] $LiAlH_4$ (16.3)	15 (−30) and 20 (0), triglyme	$SiH_4 + PH_3$ (4.3)[d] SiH_3PH_2 (7.40) $SiH_2(PH_2)_2$ (6.41) $SiH(PH_2)_3$ (3.25)
GeH_3Br (12.6) $LiAl(PH_2)_4$ (2.78)[a]	10 (−45), diglyme	GeH_4 (1.44)[c] PH_3 (0.77) GeH_3Br (0.65) $(GeH_3)_3P$ (estd 0.1) GeH_3PH_2 (9.3; 83.5% yield)

[a] Greater than 88% conversion of $LiAlH_4$ to $LiAl(PH_2)_4$. [b] Nominal quantities based on 47% conversion of $LiAlH_4$ to $LiAl(PH_2)_4$. [c] Determined by difference from the SiH_4 (GeH_4)–PH_3 mixture after complexation with BCl_3. [d] Silane and PH_3 were not separated in this experiment.

0° trap. Small amounts of yellow, nonvolatile solid remained in the reaction vessel at the end of each reaction. Owing to the intractable nature and probable high toxicity of these materials, no attempt was made to analyze these solids further. The material condensed in the −160° trap was separated by high-vacuum column distillation[9] and found to consist of the products shown in Table I. The SiH_4 (or GeH_4)–PH_3 mixtures were separated by complexation of the PH_3 with BCl_3 at −78°.

The previously reported phosphinosilane and -germane products which were characterized by comparison of their physical properties with literature values are as follows: SiH_3PH_2 (0° vapor tension: found, 484 mm; lit.[10] 487 mm; confirmed by ir and ^{1}H nmr[11] spectra), $Si_2H_5PH_2$ (0° vapor tension: found, 31.5 mm; lit.[12] 31 ± 1 mm; confirmed by ir spectrum[12]), and GeH_3PH_2 (confirmed by ir, ^{1}H nmr[11], ^{31}P nmr, and mass spectra). Other reaction products which were characterized similarly are: PH_3 (confirmed by ir[13] and mass[14] spectra), SiH_4 (confirmed by ir spectrum[15]), GeH_4 (confirmed by ir spectrum[16]), Si_2H_6 (confirmed by ir[17] and mass[18] spectra), and $(GeH_3)_3P$ (confirmed by ir and ^{1}H nmr spectra[19]).

Bis(phosphino)silane (vapor density molecular weight: calcd, 96.1; found, 96.2) melts at −112.9 ± 0.5°. Germylphosphine melts at −130.0 ± 0.5°. Tris(phosphino)silane freezes to form a glass; consequently a reproducible melting point was not obtained. The molecular weight of $SiH(PH_2)_3$ was determined mass spectrometrically.

Under reaction conditions similar to those used in the coreduction phosphination of $SiCl_4$, $GeCl_4$ was allowed to react with $LiAl(PH_2)_4$–$LiAlH_4$ solutions at temperatures as low as −45°. Voluminous quantities of an orange nonvolatile solid formed in the reaction. Phosphine, GeH_4, and GeH_3PH_2 (confirmed by ir spectrum; 1.6% yield based on $GeCl_4$) were the only volatile products which could be isolated from the reactions. No evidence for the existence of multiply PH_2-substituted germanes was obtained.

Elemental Analyses.—The decomposition of $SiH_2(PH_2)_2$ and $SiH(PH_2)_3$ for elemental analysis was accomplished by the hydrolysis of weighed samples with dilute NaOH. The calculated ratio of $SiH_x(PH_2)_{4-x}:PH_3:H_2$ (hydrolytic) according to the reaction

$$SiH_x(PH_2)_{4-x} + 2H_2O \longrightarrow SiO_2 + (4 - x)PH_3 + xH_2 \quad (x = 1 \text{ or } 2)$$

is for $SiH_2(PH_2)_2$: calcd, 1.00:2.00:2.00; found, 1.00:1.96:1.98; for $SiH(PH_2)_3$: calcd, 1.00:3.00:1.00; found, 1.00:2.94:0.97.

Vapor Pressure Data. **(A) $SiH_2(PH_2)_2$.**—Vapor pressures of $SiH_2(PH_2)_2$ in the range 0–46.4° are given in Table II and are represented by the equation

$$\log P_{\mathrm{mm}} = -\frac{1949.0}{t + 273.16} + 8.095$$

The reversibility of the curve on decreasing the temperature indicates that no significant decomposition occurred during the experiment. The extrapolated boiling boint is 103.5°, the molar heat of vaporization is 8.92 kcal, and Trouton's constant is 23.6 cal deg^{-1} mol^{-1}.

(B) $SiH(PH_2)_3$.—In an initial experiment, it was observed that measurable decomposition of $SiH(PH_2)_3$ occurred over a 7-hr period at temperatures between 24 and 75°. This was evidenced by the fact that as the temperature of the material was

---

(9) The distillation column used in this work was a 30-in., concentric-tube apparatus of the type developed in the laboratories of Professor Riley Schaeffer and coworkers, Indiana University, Bloomington, Ind.

(10) G. Fritz, *Z. Anorg. Allgem. Chem.*, **280**, 332 (1955).

(11) J. E. Drake and W. L. Jolly, *J. Chem. Phys.*, **38**, 1033 (1963).

(12) S. D. Gokhale and W. L. Jolly, *Inorg. Chem.*, **3**, 1141 (1964).

(13) P. A. Tierney, D. W. Lewis, and D. Berg, *J. Inorg. Nucl. Chem.*, **24**, 1165 (1962).

(14) Y. Wada and R. W. Kiser, *Inorg. Chem.*, **3**, 174 (1964).

(15) C. H. Tindahl, J. W. Straley, and H. N. Nielsen, *Phys. Rev.*, **62**, 151 (1942).

(16) J. W. Straley, C. H. Tindal, and H. N. Nielsen, *ibid.*, **62**, 161 (1942).

(17) G. W. Bethke and M. K. Wilson, *J. Chem. Phys.*, **26**, 1107 (1957).

(18) F. E. Saalfeld and J. H. Svec, *Inorg. Chem.*, **2**, 50 (1963).

(19) S. Craddock, E. A. V. Ebsworth, and L. A. Woodward, *J. Chem. Soc., A*, 1229 (1967).

Table II

Vapor Pressures of $SiH_2(PH_2)_2$[a]

	P, mm			P, mm	
Temp, °C	Obsd	Calcd	Temp, °C	Obsd	Calcd
0.0	9.3	9.2	33.3	54.9	55.5
9.2	16.3	15.7	39.9	74.5	75.0
16.7	23.6	23.7	46.4	97.2	96.6
21.3	30.0	30.9	27.6[b]	43.1	43.1
26.5	39.5	39.4	0.0[b]	9.3	9.2

[a] Experiment carried out over a 7-hr period. [b] Pressures observed while decreasing the temperature.

lowered, the cooling curve lay considerably higher than the heating curve. An ir spectral analysis of the sample upon completion of the experiment indicated that PH_3 had formed. Consequently, vapor pressure data were collected at four temperatures on four separate pure samples. Vapor pressures in the range 29.2–56.3° are given in Table III and are represented by the equation

$$\log P_{\text{mm}} + -\frac{2462.2}{t + 273.16} + 8.5177$$

The extrapolated boiling point is 162.9°, the molar heat of vaporization is 11.3 kcal, and Trouton's constant is 25.8 cal $\deg^{-1}$ mol^{-1}.

Table III

Vapor Pressures of $SiH(PH_2)_3$

	P, mm			P, mm	
Temp, °C	Obsd	Calcd	Temp, °C	Obsd	Calcd
29.2	2.2	2.4	49.3	7.7	7.6
40.2	4.8	4.6	56.3	11.1	11.1

(C) **GeH_3PH_2.**—Vapor pressures of GeH_3PH_2 in the range −96.3 to −49.7° are given in Table IV and are represented by the equation

$$\log P_{\text{mm}} = -\frac{1415.5}{t + 273.16} + 7.2770$$

Table IV

Vapor Pressures of GeH_3PH_2[a]

	P, mm			P, mm	
Temp, °C	Obsd	Calcd	Temp, °C	Obsd	Calcd
−96.3	0.2	0.2	−64.7	3.1	3.0
−87.4	0.5	0.5	−49.7	9.7	8.8
−83.9	0.6	0.6	−64.7[b]	3.5	3.0
−80.3	0.7	0.8	−80.2[b]	1.0	0.8
−72.0	1.6	1.7			

[a] Duration of a typical experiment, *ca.* 6 hr. [b] Pressures observed on decreasing the temperature.

Additional measurements to those given in Table IV were used in deriving this relationship. Because of the slow decomposition of GeH_3PH_2 to yield PH_3 at temperatures above *ca.* −40°, accurate vapor pressure data at temperatures above −49.7° could not be obtained. The extrapolated boiling point of GeH_3PH_2 is 48.8°, the molar heat of vaporization is 6.5 kcal, and Trouton's constant is 20.1 cal $\deg^{-1}$ mol^{-1}.

Thermal Decomposition.—Bis(phosphino)silane underwent about 5% decomposition (based on $SiH_2(PH_2)_2$ consumed) to yield PH_3 (confirmed by ir spectrum[13]) as the only volatile product when heated in a sealed tube at 95 ± 3° for 6 hr. A faint solid film formed on the wall of the reaction tube. Tris(phosphino)silane underwent 11% decomposition (based on $SiH(PH_2)_3$ consumed) when heated in a sealed tube at 70 ± 3° for 3 hr. Phosphine (confirmed by ir[13] and mass[14] spectra), trace quantities of SiH_3PH_2 (confirmed by ir spectrum[20]), and an uncharacterized nonvolatile glassy solid were the only detectable products of the pyrolysis reaction.

Results and Discussion

Phosphination Reactions.—Lithium tetraphosphinoaluminate, $LiAl(PH_2)_4$, has been found to be a highly effective phosphinating agent for the preparation of phosphinosilanes and -germanes. Monophosphinosilane (SiH_3PH_2), $Si_2H_5PH_2$, and GeH_3PH_2, which heretofore could be obtained only with difficulty and in low yields from ozonizer discharge,[12,21,22] pyrolysis,[10] ternary alloy hydrolysis,[23,24] or exchange reactions,[25] can be prepared in high yields from reactions of $LiAl(PH_2)_4$ with SiH_3Br, Si_2H_5Br, and GeH_3Br, respectively (eq 2). Multiply PH_2-substituted silanes can also be obtained from analogous reactions. Thus $SiH_2(PH_2)_2$ and $SiH(PH_2)_3$, prepared for the first time during this study, can be prepared according to

$$4RBr + LiAl(PH_2)_4 \longrightarrow AlBr_3 + LiBr + 4RPH_2 \quad (R = SiH_3,\ Si_2H_5,\ \text{or}\ GeH_3) \tag{2}$$

$$2SiH_2Br_2 + LiAl(PH_2)_4 \longrightarrow AlBr_3 + LiBr + 2SiH_2(PH_2)_2 \tag{3}$$

$$4SiHBr_3 + 3LiAl(PH_2)_4 \longrightarrow 3AlBr_3 + 3LiBr + 4SiH(PH_2)_3 \tag{4}$$

The mechanism by which phosphination of the halides occurs in the above reactions has not been determined. It is possible that phosphination occurs in a manner analogous to that proposed for the reduction of organic halides by $LiAlH_4$ in ethereal solvents.[26] Thus halide displacement by phosphinoaluminate ions of the general formula $AlH_n(PH_2)_{4-n}^-$ in a series of S_N2 reactions would be involved. However, mechanisms of halide replacement involving four-center transition states can also be considered.

In all of the phosphination reactions, formation of the desired phosphino product was accompanied by formation of small quantities of PH_3 and reduced forms of the halosilanes or -germanes. Silane, Si_2H_6, and GeH_4 were obtained in the SiH_3Br, Si_2H_5Br, and GeH_3Br phosphinations, respectively. Similarly, SiH_4 and SiH_3PH_2 and SiH_4, SiH_3PH_2, snd $SiH_2(PH_2)_2$ were produced in the SiH_2Br_2 and $SiHBr_3$ reactions, respectively.

A detailed examination of the source of PH_3 was not pursued in this study; however, it is possible that this product forms through lithium halide induced cleavage of Si–P or Ge–P bonds during the reaction, in processes similar to that described for the cleavage of Si–Si and Ge–Ge bonds.[27,28] Also, PH_3 formation as a result of silyl- or germylphosphine base displacement reactions with unreacted $LiAl(PH_2)_4$[2] cannot be discounted.

The formation of reduced and partially reduced

---

[20] H. R. Linton and E. R. Nixon, *Spectrochim. Acta*, **15**, 146 (1959).

[21] J. E. Drake and W. L. Jolly, *Chem. Ind.* (London), 1470 (1962).

[22] S. D. Gokhale and W. L. Jolly, *Inorg. Chem.*, **4**, 596 (1965).

[23] P. Royen, C. Rocktäschel, and W. Mosch, *Angew. Chem. Intern. Ed. Engl.*, **3**, 703 (1964).

[24] P. Royen and C. Rocktäschel, *Z. Anorg. Allgem. Chem.*, **346**, 290 (1966).

[25] J. E. Drake, N. Goddard, and J. Simpson, *Inorg. Nucl. Chem. Letters*, **4**, 361 (1968).

[26] L. W. Trevoy and W. G. Brown, *J. Am. Chem. Soc.*, **71**, 1675 (1949).

[27] J. S. Morrison and M. A. Ring, *Inorg. Chem.*, **6**, 100 (1967).

[28] W. R. Barnhorst and M. A. Ring, *ibid.*, **7**, 1009 (1968).

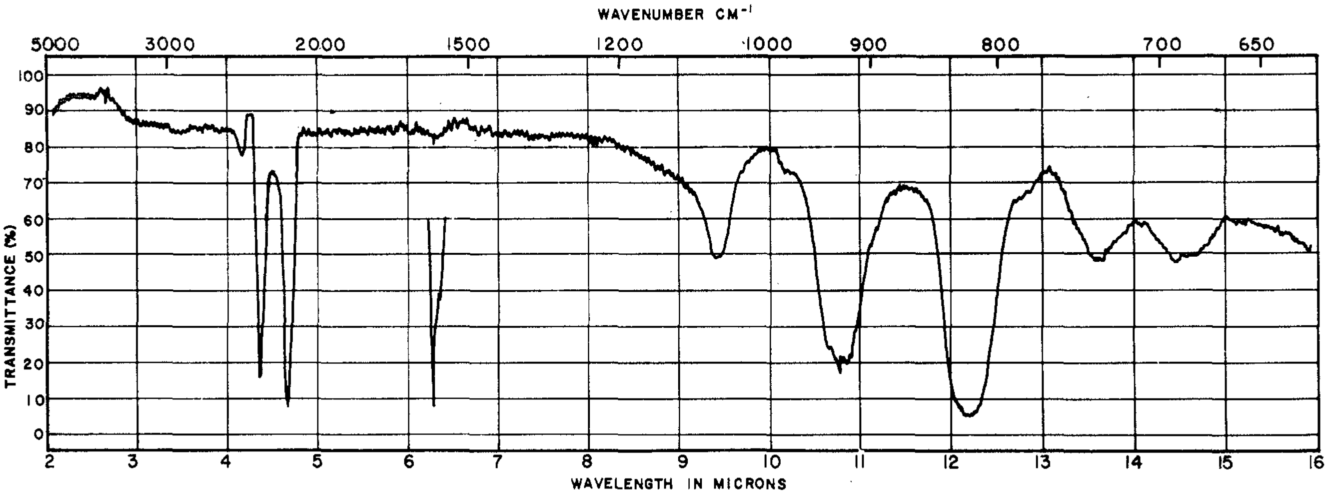

Figure 1.—Infrared absorption spectrum of $SiH_2(PH_2)_2$ (10 mm pressure in a 10-cm cell). Curve at ~1600 cm^{-1} is the polystyrene calibration.

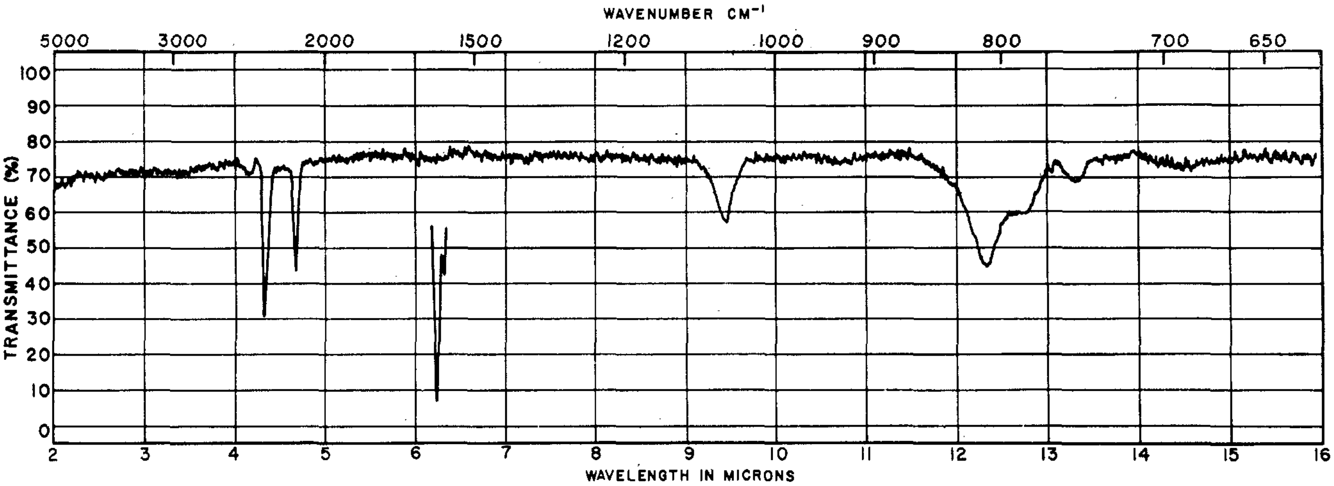

Figure 2.– Infrared absorption spectrum of $SiH(PH_2)_3$ (2 mm pressure in a 10-cm cell). Curve at ~1600 cm^{-1} is the polystyrene calibration.

products during the phosphination reactions can be attributed to the concomitant reduction of the halosilane or -germane by residual Al–H species (*e.g.*, $AlH(PH_2)_3^-$) which are invariably present in the $LiAl(PH_2)_4$ solutions. That increased quantities of reduction products were obtained in cases where $LiAlH_4$ to $LiAl(PH_2)_4$ conversion was less complete supports this premise.

In order to gain further support for the above argument and to find syntheses for $SiH_2(PH_2)_2$ and $SiH(PH_2)_3$, which could involve more readily available starting materials, solutions containing approximately equivalent quantities of what can be nominally designated at $LiAlH_4$ and $LiAl(PH_2)_4$ were allowed to react with $SiCl_4$. From this reaction SiH_4, SiH_3PH_2, $SiH_2(PH_2)_2$, and $SiH(PH_2)_3$ were obtained in high overall yield. No $(PH_2)_4Si$ was isolated. Since the products of the cophosphination reduction are readily separated, this reaction is indeed the most ideal for the preparation of $SiH_2(PH_2)_2$ and $SiH(PH_2)_3$. Attempts to prepare multiply PH_2-substituted germane from analogous cophosphination reduction reactions of $GeCl_4$ were unsuccessful. In all cases, PH_3, GeH_4, and GeH_3PH_2 were the only volatile products which were isolatable.

Bis(phosphino)silane and $SiH(PH_2)_3$ are colorless, *pyrophoric* liquids which can be maintained at room temperature and below for periods of several hours without appreciable decomposition. At temperatures above 100°, $SiH_2(PH_2)_2$ decomposes slowly to yield PH_3 and uncharacterized solid. Tris(phosphino)silane is considerably less stable, undergoing approximately 11% decomposition to PH_3, traces of SiH_3PH_2, and uncharacterized solid in 3 hr at 70°. Both $SiH_2(PH_2)_2$ and $SiH(PH_2)_3$ are rapidly hydrolyzed in aqueous media and undergo quantitative cleavage with anhydrous HCl or HBr to PH_3 and the expected halosilanes. Since these new compounds are pyrophoric and undoubtedly highly toxic, due care must be exercised in their handling.

Characterization and Properties of $SiH_2(PH_2)_2$ and $SiH(PH_2)_3$.—The characterization of the two new hydrides prepared during this study as $SiH_2(PH_2)_2$ and $SiH(PH_2)_3$ is based on elemental analyses, vapor density

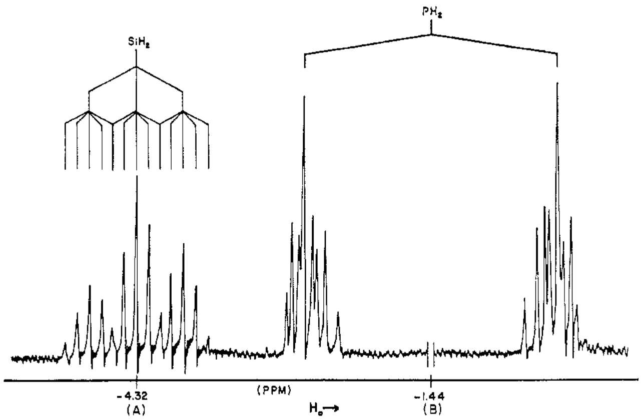

Figure 3.—Proton nmr spectrum of $SiH_2(PH_2)_2$ at 60.0 MHz.

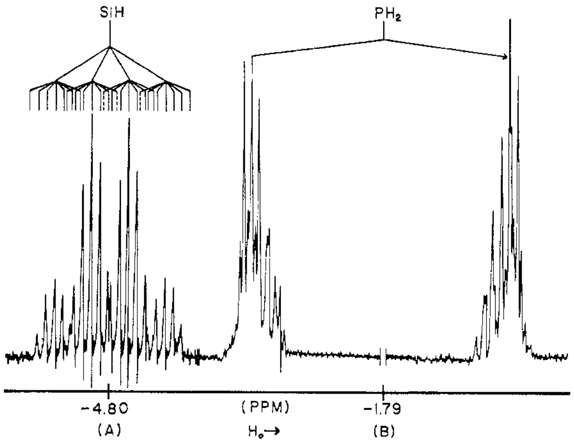

Figure 4.—Proton nmr spectrum of $SiH(PH_2)_3$ at 60.0 MHz.

molecular weight measurements (for $SiH_2(PH_2)_2$ only; molecular weight: found, 96.2; calcd, 96.1), and infrared, ^1H and ^{31}P nmr, and mass spectral data.

The mass spectra of $SiH_2(PH_2)_2$ and $SiH(PH_2)_3$ exhibit fragmentation patterns consistent with those expected for multiply PH_2-substituted silanes. The monoisotopic mass spectrum of $SiH_2(PH_2)_2$ contains peaks at (assignments in parentheses): *m/e* 28–34 (SiH_x^+ and/or PH_x^+), 59–64 ($SiPH_x^+$), and 90–96 ($SiP_2H_x^+$). The spectrum of $SiH(PH_2)_3$ exhibits peaks at (assignments in parentheses): *m/e* 28–34 (SiH_x^+ and/or PH_x^+), 59–63 ($SiPH_x^+$), 90–95 ($SiP_2H_x^+$), and 121–128 ($SiP_3H_x^+$). In the latter spectrum, very weak peaks at *m/e* 64–67, assigned to $P_2H_x^+$ ions which appear to form in the source chamber of the spectrometer, were also observed. Bis(phosphino)silane and $SiH(PH_2)_3$ exhibited molecular ions at *m/e* 96 ($^{28}SiP_2H_6^+$) and 128 ($^{28}SiP_3H_7^+$). The most intense peaks in the spectra of $SiH_2(PH_2)_2$ and $SiH(PH_2)_3$ occur at *m/e* 63 and 95, respectively, corresponding in each case to the loss of a neutral PH_2 fragment from the molecular ion.

The gas-phase infrared spectra of $SiH_2(PH_2)_2$ and $SiH(PH_2)_3$ in the region 4000–400 cm^{-1} are shown in Figures 1 and 2. The position and assignment of the absorption maxima are given in Table V. In each case, assignments are made by comparison of the data with published data and spectral assignments for other silanes, phosphines, and silylphosphines. For both $SiH_2(PH_2)_2$ and $SiH(PH_2)_3$, their formulation as simple multiply PH_2-substituted silanes is clearly consistent with the infrared data.

Table V

Infrared Absorption Maxima of $SiH_2(PH_2)$ and $SiH(PH_2)_3$ (cm^{-1})

$SiH_2(PH_2)_2$	$SiH(PH_2)_3$	Assignment	Ref
2310 s	2308 vs	P–H str	*a, b*
2160 vs	2152 s	Si–H str	*a, b*
1066 m	1062 m	PH_2 def	*c–e*
930 s		SiH_2 bend	*a, f*
823 vs	810 s	PH_2 twist	*c*
784 w	786 m	PH_2 wag	*c, e*
738 m	755 w	PH_2 twist	*c*
688 m	697 w	Unassigned	
587 w	567 m	Unassigned	
482 w	474 m	Si–P str	*d, e*

[a] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd ed, John Wiley & Sons, Inc., New York, N. Y., 1958. [b] K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," John Wiley & Sons, New York, N. Y., 1963. [c] E. R. Nixon, *J. Phys. Chem.*, **60**, 1054 (1956). [d] See ref 20. [e] See ref 12. [f] D. W. Mayo, H. E. Opitz, and J. S. Peak, *J. Chem. Phys.*, **23**, 1344 (1955).

The 60.0-MHz ^1H nmr spectra of $SiH_2(PH_2)_2$ and $SiH(PH_2)_3$ are shown in Figures 3 and 4. A summary of coupling constant and chemical shift data is given in Table VI. The spectrum of $SiH_2(PH_2)_2$ (Figure 3) consists of a 1:2:1 triplet (J_{HSiP}) of 1:4:6:4:1 pentets (J_{HSiPH}) (A, relative area 2.0) and a doublet (J_{PH}) of complex splitting (B, relative area 4.02), which can be assigned to SiH_2 and PH_2 protons, respectively. The spectrum of $SiH(PH_2)_3$ (Figure 4) exhibits a 1:3:3:1 quartet (J_{HSiP}) of 1:6:15:20:15:6:1 heptets (J_{HSiPH}) (C, relative area 1.0) and a complex doublet (J_{PH}) (D, relative area 6.04). Resonances C and D can be assigned unambiguously to SiH and PH_2 protons, respectively.

Table VI

Proton Nmr Data

	$\delta(SiH)^a$	$\delta(PH)^a$	$J_{HSiP}{}^b$	$J_{HSiPH}{}^b$	$J_{PH}{}^b$
$SiH_4{}^d$	−3.20	...	...	...	...
$SiH_3PH_2{}^e$	−3.73	−1.31	16.2 ± 0.2	5.1 ± 0.1	180 ± 1
$SiH_2(PH_2)_2$	−4.32	−1.44	18.4 ± 0.2	4.9 ± 0.1	185.5 ± 1[c]
$SiH(PH_2)_3$	−4.80	−1.79	20.4 ± 0.2	4.9 ± 0.1	196 ± 1[c]

[a] Values in parts per million relative to $(CH_3)_4Si$. [b] Values in cycles per second. [c] Distance in cycles per second between the two most intense peaks in the complex multiplets. [d] E. A. V. Ebsworth, "Volatile Silicon Compounds," Pergamon Press, New York, N. Y., 1963. [e] See ref 11.

The 40.5-MHz ^{31}P nmr spectra of $SiH_2(PH_2)_2$ and $SiH(PH_2)_3$ are shown in Figures 5 and 6. The spectra of both compounds consist of single 1:2:1 triplet resonances at δ 252 ± 3 and 216 ± 3 ppm, respectively. Because of the complex spin–spin coupling which exists in these compounds, each triplet member shows a high degree of additional splitting. The magnitudes of the splittings are indicated by the scales on each figure. Complete analyses of the ^{31}P nmr spectra have not been attempted; however, of essential importance is the fact that only one type of phosphorus atom chemical environment is present in each molecule.

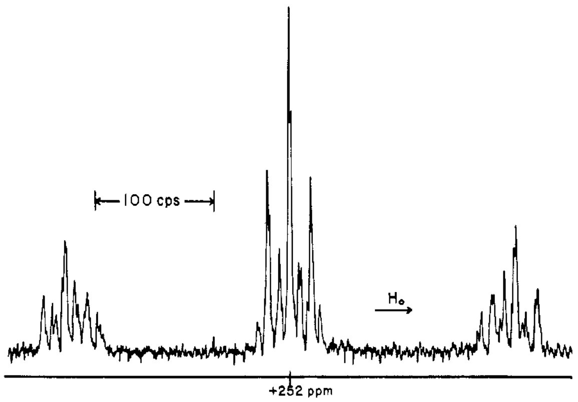

Figure 5.—Phosphorus-31 nmr spectrum of $SiH_2(PH_2)_2$ at 40.5 MHz.

It is clear from the "complex" appearances of the ^{31}P nmr spectra and the PH_2 regions of the ^1H nmr spectra that complete spectral analyses must involve considerations of "second-order" spin-spin coupling systems. The spectral patterns exhibited by $SiH_2(PH_2)_2$ and $SiH(PH_2)_3$ appear to be consistent with those expected for spin coupling systems of the types $X_2AM_2A'X'_2$ and $X_2A(X'_2A')MA''X''_2$, respectively; however, the analyses of these spectra are beyond the scope of this paper and are being reported in detail elsewhere.[29]

An examination of the data shown in Table VI for the series SiH_4, SiH_3PH_2, $SiH_2(PH_2)_2$, and $SiH(PH_2)_3$ indicates that distinct trends exist in certain of the coupling constant and chemical shift values. It is evident that the successive replacement of H atoms on Si by PH_2 groups results in a increase in the HSiP coupling constants and that the SiH and the PH_2 proton(s) undergo a monotonic downfield chemical shift. Any attempt to explain these trends is complicated by the uncertainties which exist concerning the bonding and structure in these systems. Also, attempts to explain coupling constant and/or chemical shift trends of atoms or groups bound to silicon have not in general been completely satisfactory.[30] However, the downfield chemical shift of the SiH proton(s) upon increased PH_2 substitution is particularly interesting since the trend in this system can be compared with those reported for halosilane series of the type SiH_nX_{4-n}. In the chlorosilane series the downfield trend in chemical shift might be attributed to the increased inductive effect as the hydrogens are replaced by the more electronegative chlorine atoms. However, in the fluorosilane series where an upfield shift is observed, it is clear that this explanation does not suffice. Similarly, in the phosphinosilane series a simple inductive-effect argument is inadequate since the electronegativity of phosphorus ($\chi = 2.06$) is essentially the same as that of hydrogen ($\chi = 2.10$).[31] Thus it would appear that an explanation for the observed trend in chemical shifts of the SiH proton(s) for series of substituted silanes is complex and is primarily based on magnetic anisotropy and/or paramagnetic effects.

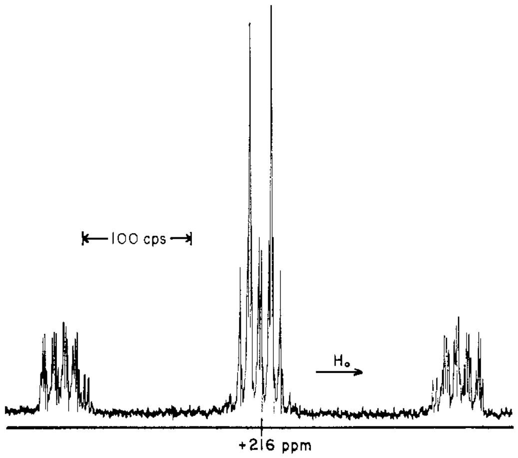

Figure 6.—Phosphorus-31 nmr spectrum of $SiH(PH_2)_3$ at 40.5 MHz.

A complete investigation of the chemistry of these new multiply PH_2-substituted silanes is currently in progress in our laboratories and will be reported later.

Acknowledgment.—Partial support of this work by a University of Colorado Council on Research and Creative Work summer fellowship for A. D. N., a National Defense Education Act Title IV fellowship for D. C. W., and a gift of germanium chemicals from the Germanium Research Center are gratefully acknowledged.

---

(29) R. A. Newmark and A. D. Norman, to be submitted for publication.

(30) E. A. V. Ebsworth, "Volatile Silicon Compounds," Pergamon Press, New York, N. Y., 1963, and references cited therein.

(31) A. Allred and E. Rochow, *J. Inorg. Nucl. Chem.*, **5**, 264, 269 (1958).