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The Preparation and Properties of Methyl(phosphino)silanes and -germanes[1]

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A series of new methyl(phosphino)germanes and -silanes—$(CH_3)_3GePH_2$, $(CH_3)_2Ge(PH_2)_2$, and $(CH_3)_2Si(PH_2)_2$—has been synthesized by the reaction of $LiAl(PH_2)_4$ with the appropriate halogermane or -silane. The previously reported $(CH_3)_3SiPH_2$ has also been obtained in high yield. Mixed reduction–phosphination products, $(CH_3)_2Ge(PH_2)H$ and $(CH_3)_2Si(PH_2)H$, have been prepared by the reaction of nominally equimolar $LiAlH_4$–$LiAl(PH_2)_4$ mixtures with $(CH_3)_2GeCl_2$ and $(CH_3)_2SiCl_2$, respectively. The new compounds have been characterized by elemental analyses, molecular weight measurements, and vapor tension data. Proton and ^{31}P nmr, ir, and mass spectral data are also reported for the compounds.

Introduction

The preparation and characterization of the new methyl(phosphino)silanes and -germanes were carried out in connection with a program involving reactions of silicon–phosphorus and germanium–phosphorus compounds with boranes. In this study, both mono- and bisphosphino derivatives were needed. Because of our recent success in preparing unsubstituted phosphinosilanes and -germanes by direct phosphination of halosilanes and -germanes with $LiAl(PH_2)_4$[2–4] and the importance of establishing the generality of this phosphination method, this reaction was used to prepare the compounds of interest. Three new monophosphino compounds, $(CH_3)_3GePH_2$, $(CH_3)_2Ge(PH_2)H$, and $(CH_3)_2Si(PH_2)H$, and the previously reported $(CH_3)_3SiPH_2$[5] have been prepared in high yields. Also, two new bisphosphino compounds, $(CH_3)_2Si(PH_2)_2$ and $(CH_3)_2Ge(PH_2)_2$, have been obtained.

Results

Trimethylsilylphosphine and $(CH_3)_3GePH_2$ are formed in high yield from reactions of $(CH_3)_3SiCl$ and $(CH_3)_3GeCl$, respectively, with triglyme solutions of $LiAl(PH_2)_4$ (eq 1). Similarly, reactions of $(CH_3)_2SiCl_2$

$$4(CH_3)_3MCl + LiAl(PH_2)_4 \longrightarrow LiCl + AlCl_3 + 4(CH_3)_3MPH_2 \quad (1)$$

and $(CH_3)_2GeCl_2$ with $LiAl(PH_2)_4$ yield the bisphosphino compounds, $(CH_3)_2Si(PH_2)_2$ and $(CH_3)_2Ge(PH_2)_2$ (eq 2). In every reaction, formation of the

$$2(CH_3)_2MCl_2 + LiAl(PH_2)_4 \longrightarrow LiCl + AlCl_3 + 2(CH_3)_2M(PH_2)_2 \quad (M = \text{Si or Ge}) \quad (2)$$

desired product is accompanied by small quantities of the reduced halide and varying quantities of PH_3. Reduction of the halosilane or -germane concomitant with phosphination is not unexpected since the $LiAl(PH_2)_4$ solutions invariably contained a small quantity (<5%) of residual Al–H bonded materials. Phosphine may form as a result of aluminum halide promoted disproportionation of the phosphino products similar to that observed with boron halides.[6,7] Also, lithium halide induced cleavage of Si–P or Ge–P bonds in a manner analogous to that observed for Si–Si and Ge–Ge bonds[8,9] cannot be discounted. Further studies are necessary before the source(s) of PH_3 in the phosphination reactions can be ascertained clearly.

Reactions of nominally $LiAl(PH_2)_4$–$LiAlH_4$ mixtures with dimethylsilyl and dimethylgermyl chlorides results in the formation of mixed phosphination–reduction products. Thus, the cophosphination reduction of $(CH_3)_2SiCl_2$ and $(CH_3)_2GeCl_2$ resulted in the formation of two new monophosphino compounds, $(CH_3)_2Si(PH_2)H$ and $(CH_3)_2Ge(PH_2)H$, respectively, along with the expected $(CH_3)_2SiH_2$, $(CH_3)_2Si(PH_2)_2$, $(CH_3)_2GeH_2$, and $(CH_3)_2Ge(PH_2)_2$.

Under the mild reaction conditions used in this study, the formation of trace quantities of bis- and/or tris-substituted phosphines, $[(CH_3)_3Si]_2PH$ and/or $[(CH_3)_3Si]_3P$, was observed only in the phosphination of $(CH_3)_3SiCl$. Although somewhat larger quantities of these products were observed by Finholt, *et al.*, in a 9-hr reaction at room temperature,[10] the tendency toward formation of these products appears to be markedly less in the $LiAl(PH_2)_4$ phosphinations than in dihydrogen phosphide–silyl halide reactions. The $LiPH_2$–$(CH_3)_3SiCl$ reaction yields approximately equimolar quantities of $(CH_3)_3SiPH_2$, $[(CH_3)_3Si]_2PH$, and $[(CH_3)_3Si]_3P$[5] and the $NaPH_2$–$(CH_3)_3SiCl$ reaction results in $[(CH_3)_3Si]_3P$ as the main product.[11] Analogous reactions involving SiH_3Br also yield exclusively $(SiH_3)_3P$[11,12] except under specially controlled conditions in which some $(SiH_3)_2PH$ and SiH_3PH_2 can be obtained.[13] As has been pointed out recently, by Glidwell and Sheldrick,[13] the MPH_2 reactions probably yield large quantities of bis- and tris-substituted products as a result of the formation of nucleophilic intermediate silylphosphide anions (*i.e.*, SiH_3PH^- and $(SiH_3)_2P^-$) which can in turn react with the silyl halide. In these reactions, formation of the intermediate anions probably results

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TABLE I

INFRARED ABSORPTION MAXIMA[a] AND ASSIGNMENTS

$(CH_3)_3GePH_2$[b]	$(CH_3)_2(PH_2)H$[c]	$(CH_3)_2Ge(PH_2)_2$[d]	$(CH_3)_2Si(PH_2)_2$[e]	$(CH_3)_2Si(PH_2)H$[f]	Assignments
2976 s	2976 m	2967 s	2958 m	2994 m	CH_3 asym str[g,h]
2899 s	2915 m	2899 s	2890 w	2924 w	CH_3 sym str[g,h]
2294 s	2294 s	2294 vs	2285 s	2309 s	PH str[g,h]
				2138 vs	SiH str[g,h]
					GeH str[g,h]
	2079 vs				
1852 w	1845 w				
1815 w					
1416 m	1414 w	1414 w	1412 w	1418 m	CH_3 asym def[g,l]
1241 s	1244 m	1236 m	1253 m	1257 s	CH_3 sym def[g,l]
1065 m	1067 m	1064 s	1060 m	1062 m	PH_2 def[i,k]
870 m, sh	855 s, sh	870 w	841 s	880 vs	
830 vs	838 vs	836 s	830 vs	842 s	
		810 vs	820 s	813 m	
			795 m	795 m	SiC str[g]
770 m	772 m		767 w, sh	778 m	PH_2 wag[i,k]
				729 w	
				712 m	
	698 m		695 m	700 w	
641 w		639 w	650 m	660 m	
621 s, sh			620 w		
613 vs				608 m	
	604 s, sh	600 m			Ge–C str
585 m	587 vs	579 m			
577 s	576 s, sh				
				583 s	
				545 m	
				478	Si–P str[j,k]
			470 s	470	

[a] All absorption maxima are in cm^{-1} units. Abbreviations: vs, very strong; s, strong; m, medium; w, weak; vw, very weak; sh, shoulder. [b] Sample pressure 15 mm. [c] Sample pressure 13 mm. [d] Sample pressure 4 mm. [e] Sample pressure 13 mm. [f] Sample pressure 15 mm. [g] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd ed, John Wiley and Sons, New York, N. Y., 1958. [h] K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," John Wiley and Sons, New York, N. Y., 1963. [i] E. R. Nixon, *J. Phys. Chem.*, **60**, 1054 (1956). [j] H. R. Linton and E. R. Nixon, *Spectrochim. Acta*, **15**, 146 (1958). [k] S. D. Gokhale and W. L. Jolly, *Inorg. Chem.*, **3**, 1141 (1964). [l] R. J. Cross and F. Glockling, *J. Organometal. Chem.* (Amsterdam), **3**, 146 (1965).

from reaction of SiH_3PH_2 and $(SiH_3)_2PH$ with the highly basic PH_2^- species. However, it is possible that the $Al(PH_2)_4^-$ ion is less basic than PH_2^-, and as a result, significant quantities of intermediate silylphosphide anions are not found in the $LiAl(PH_2)_4$ phosphinations. However, the lower basicity does not preclude the phosphination reaction since this could occur *via* a mechanism involving a four-center transition state.

The compounds prepared in this study, excepting $(CH_3)_3SiPH_2$, were characterized on the basis of elemental analyses, vapor tension data, and, where possible, vapor tension molecular weights. Characterization data were also obtained from infrared, ^1H and ^{31}P nmr, and mass spectral data. Elemental analyses of the germylphosphines were obtained routinely; however, owing to the high reactivity of the silylphosphines toward air and moisture these compounds were analyzed by quantitative measurement in the vacuum system of the products of HCl-cleavage reactions.

The mass spectra of the five new phosphino compounds exhibited fragmentation patterns consistent with those expected for PH_2-substituted methylsilanes and methylgermanes. In each case a weak molecular ion was observed, providing confirmation of the molecular weight and compound stoichiometry.

The infrared spectral data and tentative peak assignments are given in Table I. The spectra of $(CH_3)_3GePH_2$, $(CH_3)_2Ge(PH_2)H$, and $(CH_3)_2Ge(PH_2)_2$ show absorptions at 2294 cm^{-1} and in the range 2899–2976 cm^{-1}, characteristic of CH_3 group C–H stretching and P–H stretching modes, respectively. In addition a strong characteristic Ge–H stretching absorption at 2079 cm^{-1} is present in the $(CH_3)_2Ge(PH_2)H$ spectrum. The spectra of $(CH_3)_2Si(PH_2)H$ and $(CH_3)_2Si(PH_2)_2$ exhibit characteristic P–H and CH_3 group C–H stretching absorptions in the ranges 2285–2309 and 2890–2994 cm^{-1}, respectively. The $(CH_3)_2Si(PH_2)H$ shows a strong Si–H stretching absorption at 2138 cm^{-1}. In addition, these latter compounds show absorptions at 470–478 cm^{-1} which can be assigned to the Si–P bond stretching mode.

Chemical shift and coupling constant data obtained from the ^1H nmr spectra of the phosphines prepared in this study are given in Table II. The ^1H nmr spectrum of $(CH_3)_3GePH_2$ consists of two doublets, areas 9 and 2, which can be assigned to CH_3 and PH_2 protons, respectively. Dimethylsilylphosphine and $(CH_3)_2Ge(PH_2)H$ exhibit three resonances: an apparent triplet (area 6) due to the CH_3 protons, a doublet of septets (area 1) due to the H on the Si or Ge atom, and a widely spaced 1:2:1 doublet of doublets (area 2) from

TABLE II

NUCLEAR MAGNETIC RESONANCE DATA

Measurement	$(CH_3)_2Si(PH_2)H$	$(CH_3)_2Si(PH_2)_2$	$(CH_3)_3GePH_2$	$(CH_3)_2Ge(PH_2)H$	$(CH_3)_2Ge(PH_2)_2$
		^1H Nmr Data[a]			
$\delta(CH)$[b]	-0.32	-0.52	-0.40	-0.47	-0.67
$\delta(MH)$	-4.36	...	...	-4.32	...
$\delta(PH_2)$	-1.22	-1.50	-1.24	-1.32	-1.58
J_{HCMH}[c]	4.0 ± 0.1	...	...	3.9 ± 0.1	...
J_{HCMP}	3.9 ± 0.1	3.9 ± 0.2	3.3 ± 0.2	3.3 ± 0.2	3.3 ± 1
J_{PH}	182 ± 1	187 ± 1[e]	177 ± 1	176 ± 1	180 ± 1[e]
J_{HMP}	21.5 ± 0.2	...	...	21.0 ± 0.2	...
J_{HPMH}	4.2 ± 0.1	...	...	$4.1 + 0.1$	...
		^{31}P Nmr Data			
$\delta(P)$[d]	244 ± 3	220 ± 3	236 ± 3	243 ± 3	222 ± 3

[a] Obtained on 10–20% (by volume) solutions in $(CH_3)_4Si$. [b] Chemical shift in ppm relative to internal $(CH_3)_4Si$. [c] Coupling constants in Hz. [d] Chemical shift in ppm relative to 85% H_3PO_4. [e] Distance between the two most intense peaks in the complex multiplet.

the PH_2 protons. The CH_3 resonances in these spectra apparently appear as triplets due to the equivalence of J_{HCMH} and J_{HCMP}. The spectra of $(CH_3)_2Si(PH_2)_2$ and $(CH_3)_2Ge(PH_2)_2$ consist of 1:2:1 triplet (area 6) and complex doublet (area 4) resonances which are attributable to CH_3 and PH_2 protons, respectively.

The ^{31}P nmr spectrum of each compound exhibits a widely spaced 1:2:1 triplet, consistent with that expected from molecules containing mono- or bis-PH_2 group substitution. Each triplet member shows the expected fine structure due to coupling between the ^{31}P nuclei and other protons in the system. Owing to the chemical equivalence but magnetic nonequivalence of the P and H nuclei of the PH_2 groups, resonances arising from these nuclei exhibit complex "second-order" splitting. The PH_2 proton region of the ^1H nmr spectra and the ^{31}P spectra can be analyzed in terms of spin–spin coupling systems of the $AX_2A'X'_2$ type. This analysis is beyond the scope of this paper and will be reported elsewhere.[14]

The phosphinosilanes and -germanes prepared in this study are colorless liquids which are sensitive to air and moisture. Dimethylbis(phosphino)silane and $(CH_3)_2Si(PH_2)H$ are highly pyrophoric. Although the compounds react readily with oxygen or water, with the exception of $(CH_3)_2Ge(PH_2)_2$, they are thermally stable for periods of several hours at room temperature. The products of the thermal decomposition of $(CH_3)_2Ge(PH_2)_2$ are being investigated currently and will be reported later.

Based on the results of this study and the one reported previously, it appears that the $LiAl(PH_2)_4$ phosphination reaction can be considered general for the synthesis of phosphinosilanes and -germanes of both substituted and unsubstituted types. Although no attempt was made to prepare tris(phosphino)alkylsilanes or -germanes in this study, our previous report of the preparation of $SiH(PH_2)_3$ makes it reasonable to assume they could be prepared. Also, Finholt, *et al.*,[10] have shown that high yields of ethylphosphine can be obtained from the phosphination of ethyl chloride. Thus since PH_2 bonds can be formed to C, Si, and Ge, it seems plausible that other phosphino–metalloid and –metal compounds may be prepared similarly. Further work is necessary before the entire scope of the $LiAl(PH_2)_4$ phosphination method can be evaluated completely.

Experimental Section

Apparatus.—All work was carried out in a conventional, high-vacuum system.[15,16] 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 4–7 hr. Melting points were obtained by the Stock magnetic plunger technique. Mass spectra were obtained on an Atlas CH-5 spectrometer. Infrared spectra in the range 4000–400 cm^{-1} were recorded with Perkin-Elmer Model 21 and 137G spectrometers on gaseous samples in 10-cm KBr cells. Proton nuclear magnetic resonance spectra were obtained at 60.0 MHz using a Varian Associates A-60A spectrometer. Phosphorus-31 spectra were obtained at 40.5 MHz using the HA-100 spectrometer. All spectra were obtained in the high-resolution mode and were calibrated using the integrator-audiofrequency side bands.

Materials.—Phosphine[17] and $(CH_3)_3GeCl$[18] were prepared and purified by published methods. Trimethylsilyl chloride, $(CH_3)_2SiCl_2$, and $(CH_3)_2GeCl_2$ (Alfa Inorganics) were distilled under N_2 and finally purified by fractional condensation techniques. Lithium tetrahydroaluminate ($LiAlH_4$) was recrystallized from diethyl ether and stored under dry nitrogen. Triglyme (1,2-bis(2-methoxyethoxy)ethane) was distilled at reduced pressure from $LiAlH_4$ prior to use.

Preparation of $LiAl(PH_2)_4$ Solutions.—The $LiAl(PH_2)_4$ solutions and nominally $LiAlH_4$–$LiAl(PH_2)_4$ solutions were prepared from the reaction of PH_3 with $LiAlH_4$ in triglyme during 48–96 hr essentially as described by Finholt, *et al.*[10] (eq 3). The solutions used in the cophosphination–reduction reactions were prepared by allowing the quantity of PH_3 indicated in Table III to react with $LiAlH_4$. For convenience these solutions are described as containing nominal percentage quantities of $LiAlH_4$ and $LiAl(PH_2)_4$; however, it is recognized that in fact the solutions undoubtedly consist of a complex mixture of $LiAlH_n(PH_2)_{4-n}$ species.

$$4PH_3 + LiAlH_4 \longrightarrow LiAl(PH_2)_4 + 4H_2 \qquad (3)$$

Syntheses of the Methyl(phosphino)silanes and -germanes.—Reaction conditions for typical syntheses of the phosphinosilanes and -germanes are shown in Table III. In each case the halosilane or -germane was condensed at −196° into a 1-l. bulb containing solutions of $LiAl(PH_2)_4$ or $LiAlH_4$–$LiAl(PH_2)_4$. The

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TABLE III

TYPICAL SYNTHESES OF METHYL(PHOSPHINO)SILANES AND -GERMANES

Reactants (mmol)	Time, min (temp, °C)	Products (mmol)
$(CH_3)_3SiCl$ (5.86) $LiAl(PH_2)_4$ (2.90)^a	20 (−10)	PH_3 (3.84) $(CH_3)_3SiH$ (0.22) $(CH_3)_3SiPH_2$ (4.72; 80% yield)
$(CH_3)_2SiCl_2$ (8.62) $LiAl(PH_2)_4$ (7.15)^a	10 (−23), 20 (−10)	PH_3 (2.10) $(CH_3)_2SiH_2$ (0.49) $(CH_3)_2Si(PH_2)H^b$ (0.43) $(CH_3)_2Si(PH_2)_2{}^b$ (5.15; 60% yield)
$(CH_3)_2SiCl_2$ (3.85) $\left.\begin{array}{l}LiAl(PH_2)_4\\LiAlH_4\end{array}\right\}(4.20)^c$	10 (−30), 20 (−10)	$PH_3{}^b$ (1.08) $(CH_3)_2SiH_2$ (0.68) $(CH_3)_2Si(PH_2)H^b$ (1.40; 36% yield) $(CH_3)_2Si(PH_2)_2{}^b$ (1.12)
$(CH_3)_3GeBr$ (3.10) $LiAl(PH_2)_4$ (2.91)^a	25 (−23), 10 (0)	PH_3 (3.30) $(CH_3)_3GeH$ (0.31) $(CH_3)_3GePH_2{}^b$ (2.35; 76% yield)
$(CH_3)_2GeCl_2$ (5.83) $LiAl(PH_2)_4$ (4.55)^a	15 (−23), 20 (0)	PH_3 (1.51) $(CH_3)_2GeH_2$ (0.55) $(CH_3)_2Ge(PH_2)H^b$ (0.61) $(CH_3)_2Ge(PH_2)_2{}^b$ (3.08; 53% yield)
$(CH_3)_2GeCl_2$ (4.08) $\left.\begin{array}{l}LiAl(PH_2)_4\\LiAlH_4\end{array}\right\}(3.91)^d$	20 (−30), and 10 (−10)	$PH_3{}^b$ (1.38) $(CH_3)_2GeH_2$ (0.75) $(CH_3)_2Ge(PH_2)H^b$ (1.72) $(CH_3)_2Ge(PH_2)_2{}^b$ (0.91)

[a] Greater than 92% conversion of $LiAlH_4$ to $LiAl(PH_2)_4$. [b] Characterized in this study. [c] Nominally 60% $LiAl(PH_2)_4$–40% $LiAlH_4$. [d] Nominally 65% $LiAl(PH_2)_4$–35% $LiAlH_4$.

TABLE IV

VAPOR PRESSURE *vs.* TEMPERATURE DATA

$(CH_3)_3GePH_2$			$(CH_3)_2Ge(PH_2)H$			$(CH_3)_2Si(PH_2)H$			$(CH_3)_2Si(PH)_2$		
	P, mm			*P*, mm			*P*, mm			*P*, mm	
Temp, °C	Obsd	Calcd	Temp, °C	Obsd	Calcd	Temp, °C	Obsd	Calcd	Temp, °C	Obsd	Calcd
0.0	18.6	18.5	−17.0	9.4	9.4	−30.7	11.4	11.8	0.0	3.3	3.4
9.7	30.0	30.3	−5.6	19.1	19.1	−20.0	22.5	22.9	6.0	4.7	4.9
15.3	38.8	39.5	0.0	26.5	26.5	−13.7	32.9	32.9	11.6	7.0	7.0
21.8	53.4	53.4	4.2	34.3	33.7	−9.0	42.6	42.4	17.5	10.1	9.9
29.0	73.9	73.3	9.7	45.4	45.4	0.0	68.7	68.3	28.0	17.9	17.9
34.5	91.8	92.2	15.3	60.3	61.0	7.5	99.7	98.9	34.2	25.8	24.9
40.7	118.3	118.7	19.8	75.8	76.5	12.2	123.5	123.1	41.0	35.5	35.1
45.9	145.2	145.2	0.0	26.6^a	26.5	14.3	136.3	136.1	47.4	48.7	48.0
0.0	18.7	18.5^a				16.7	150.5	151.1	54.6	67.1	67.1
						0.0	69.1^a	68.3	20.4	11.8	11.7
									0.0	3.5^a	3.4

[a] Pressure obtained upon decreasing the temperature.

stirred reaction mixture was allowed to warm from −196° and react for the indicated time. Upon completion of the reaction, volatile products were pumped into the vacuum line and passed through traps maintained at *ca.* −5° (ice–salt slush) and −160° into a −196° trap. Triglyme solvent and PH_3 condensed at −5 and −196°, respectively. The material in the −160° trap consisted mainly of methylsilane or -germane and the desired phosphine product(s). This fraction was separated by high-vacuum column distillation.[19] The quantities of products obtained in each reaction are given in Table III. Small amounts of yellow-orange nonvolatile solids were also formed in each reaction; however, these solids were not analyzed further.

Known reaction products were characterized by comparison of their physical and spectral properties with literature values: PH_3 confirmed by ir[20] and mass[21] spectra; $(CH_3)_3SiH$, confirmed by ir spectrum;[22] $(CH_3)_3SiPH_2$, confirmed by ir and ^1H nmr spectra;[5] $(CH_3)_2SiH_2$, confirmed by ir spectrum;[22] $(CH_3)_3GeH$, confirmed by ir spectrum;[23] and $(CH_3)_2GeH_2$, confirmed by ir spectrum[24] and vapor tension.[25]

Analytical Data.—Analytical data[26] for the methyl(phosphino)germanes were as follows. *Anal.* Calcd for $(CH_3)_3GePH_2$ [$C_3H_{11}GeP$]: C, 23.91; H, 7.36; P, 20.55; mol wt, 150.68. Found: C, 23.78; H, 7.33; P, 20.70; mol wt (vapor density), 150.9. Calcd for $(CH_3)_2Ge(PH_2)H$ [C_2H_9GeP]: C, 17.58; H, 6.64; P, 22.66; mol wt, 136.65. Found: C, 17.55; H, 6.58; P, 23.00; mol wt (vapor density), 137.1. Calcd for $(CH_3)_2Ge(PH_2)_2$ [$C_2H_{10}GeP_2$]: C, 14.24; H, 5.98; P, 36.73. Found: C, 14.30; H, 5.98; P, 35.73.

The decomposition of $(CH_3)_2Si(PH_2)_2$ and $(CH_3)_2Si(PH_2)H$ for elemental analyses was accomplished by the reaction of weighed

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(19) The distillation column used in this work was a 30-in. concentric-type apparatus of the type developed in the laboratories of Professor Riley Schaeffer and coworkers, Indiana University, Bloomington, Ind.; see also D. F. Shriver, "The Manipulation of Air Sensitive Compounds," McGraw-Hill Book Co., Inc., New York, N. Y., 1969, p 90.

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Table V

Physical Constants of the Methyl(phosphino)silanes and -germanes

Compound	Mp, °C	Bp,[a] °C	ΔHv,[b] kcal mol^{-1}	Trouton constant	Vapor pressure equation constants[c] *A*	*C*	Temp range, °C
$(CH_3)_3GePH_2$	−97.2	95.8	7.762	21.0	−1696.2	7.4784	0–45.9
$(CH_3)_2Ge(PH_2)H$	−106.5	74.2	8.526	24.5	−1863.3	8.2458	−17.0–19.8
$(CH_3)_2Si(PH_2)_2$	−108.0	117.9	9.766	25.0	−2134.1	8.3384	0.0–54.6
$(CH_3)_2Si(PH_2)H$	−116.6	54.7	7.519	22.8	−1643.0	7.8491	−30.7–14.3
$(CH_3)_2Ge(PH_2)_2$[d]	−100.2	...	...	...	...	...	...

[a] Calculated from the vapor pressure equation. [b] Calculated from the slope of a log P_{mm} *vs.* t^{-1} plot. [c] For the equation log $P_{mm} = [A/(t + 273.16)] + C$. [d] Too unstable for a vapor pressure *vs.* temperature determination.

samples with anhydrous HCl. The calculated ratio of $(CH_3)_2SiH_x(PH_2)_{2-x}:PH_3:(CH_3)_2SiH_xCl_{2-x}$ according to the reaction

$$(CH_3)_2SiH_x(PH_2)_{2-x} + (2-x)HCl \longrightarrow (2-x)PH_3 + (CH_3)_2SiH_xCl_{2-x} \qquad (x = 0, 1)$$

is as follows: for $(CH_3)_2Si(PH_2)H$: calcd, 1.00:1.00:1.00; found, 1.00:0.97:0.94; for $(CH_3)_2Si(PH_2)_2$: calcd, 1.00:2.00:1.00; found, 1.00:1.92:0.95. The PH_3,[11,20] $(CH_3)_2SiCl_2$,[27,28] and $(CH_3)_2SiHCl$[29,30] which formed in the reactions were confirmed by ir spectra and vapor tension data.

Vapor Pressure Data.—Vapor pressures of the phosphinosilanes and -germanes are given in Table IV. Melting points and the physical constants obtained from the vapor pressure data are given in Table V. Data were not obtained for $(CH_3)_2Ge(PH_2)_2$ since decomposition to yield PH_3 and uncharacterized solids was too rapid in the temperature range required for vapor tension measurements.

Mass Spectra.—Mass spectra were obtained at an ionizing voltage of 70 eV. All spectra were obtained after the sample inlet chamber has been pretreated with the desired phosphinosilane or -germane for a period of 10–15 min.

All of the compounds characterized in this study exhibited the expected mass spectral fragmentation patterns. Fundamental spectral data for the compounds are: $(CH_3)_2Si(PH_2)H$, highest mass peak at *m/e* 94 (relative intensity 0.7% of the major peak at *m/e* 59) assigned to the $(CH_3)_2{}^{30}Si(PH_2)H^+$ molecular ion; $(CH_3)_2Si(PH_2)_2$, highest mass peak at *m/e* 126 (relative intensity 0.6% of the major peak at *m/e* 91) assigned to the $(CH_3)_2{}^{30}Si(PH_2)_2{}^+$ molecular ion; $(CH_3)_3GePH_2$, highest mass peak at *m/e* 154 (relative intensity 0.8% of the major peak at *m/e* 119) assigned to the $(CH_3)_3{}^{76}GePH_2{}^+$ ion; $(CH_3)_2Ge(PH_2)H$, highest mass peak at *m/e* 140 (relative intensity 6.4% of the major peak at *m/e* 105) attributed to the $(CH_3)_2{}^{76}Ge(PH_2)H^+$ ion; and $(CH_3)_2Ge(PH_2)_2$, highest mass peak at *m/e* 172 (relative intensity 1.7% of the major peak at *m/e* 137) attributed to the $(CH_3)_2{}^{76}Ge(PH_2)_2{}^+$ molecular ion.

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The Electronic Energies and Structure of Difluoroborane

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The electronic energy and distribution of difluoroborane, HBF_2, are examined by molecular quantum chemical calculations using Gaussian-type atomic orbitals. The structure of HBF_2 is investigated and excellent agreement with the experimental parameters is obtained. The π-localization and reorganization energies of difluoroboranes are calculated to be 35.7 and 24.4 kcal/mol, respectively.

Introduction

The preparation of difluoroborane (HBF_2) was first reported in 1964.[1] It has since been subjected to a thorough physical examination by infrared,[2–6] nuclear magnetic resonance,[7,8] and microwave[9] spectroscopy. There is very little information, however, concerning the electronic structure and energy of this compound. In this publication the results of calculations on this compound are reported giving details of the electronic structure and energy.

Results and Discussion

Calculations.—The calculations have been performed within the framework of LCAO-MO-SCF theory using Gaussian orbitals[10] as the basis set. The

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