bonds and what are thought to be largely amine hydrogen difluoride salts.[1b,8] The reaction resulted in the formation of a new heterocyclic system in good yield in the one case. It is possible that a polymeric material also resulted, though the reaction in this case was run to optimize ring formation by limiting the quantity of methylamine available. When dimethylamine is used, the second methyl group effectively blocks ring or polymer formation and the observed singly substituted straight-chain product was formed. Surprisingly, no disubstituted product was recovered when higher amine:ligand ratios were used. Instead, increasing quantities of $(CH_3)_2NPF_2$ were observed suggesting that the formation of $(CH_3)_2NPFCH_2CH_2PFN(CH_3)_2$ is at least accompanied by P–C bond breakage. It is possible that $(CH_3)_2NPFCH_2CH_2PFN(CH_3)_2$ is sufficiently nonvolatile to have remained with the hydrogen difluoride salts in the solid residue where its presence would be very difficult to confirm. The unexpected observation of $(CH_3)_2NPF_2$ at higher stoichiometric ratio may be due to a kinetic effect; *i.e.*, formation of $(CH_3)_2NPF_2$ may be higher order in $HN(CH_3)_2$ than is formation of $(CH_3)_2NPFCH_2CH_2PF_2$. Alternately, the initial formation of $F_2PCH_2CH_2PFN(CH_3)_2$ could affect the opposite difluorophosphino group such that the P–C bond becomes susceptible to bond cleavage by $HN(CH_3)_2$. The product isolated should be of interest in its coordinating properties as either five- or six-membered chelate rings may form depending on whether the bonding is through the two phosphorus atoms or through phosphorus and the nitrogen atom. Further, the PF_2 group is expected to be a better π-acceptor site than is the PFN group while the PFN site is expected to be a better σ donor. We are, at present, investigating these possibilities.

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Registry No. $(CH_3)_2NPFCH_2CH_2PF_2$, 52810-60-3; $FPCH_2CH_2PFNCH_3$, 52810-61-4; $PF_2CH_2CH_2PF_2$, 50966-32-0; $HN(CH_3)_2$, 124-40-3; H_2NCH_3, 74-89-5; NH_3, 7664-41-7; ^{31}P, 7723-14-0.

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Reaction of Silicon Difluoride with Phosphine

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The cocondensation reaction of silicon difluoride and phosphine yields the new compounds difluorosilylphosphine, SiF_2HPH_2, and trifluorosilylphosphine, SiF_3PH_2. Proton and fluorine nmr parameters and mass spectroscopic data are presented. The reaction also yields pentafluorodisilane and higher molecular weight compounds which are thermally unstable. Improvement in the resolution of the ^{19}F nmr spectrum of Si_2F_5H is reported.

Introduction

Since 1965, the chemistry of the high-temperature species silicon difluoride, SiF_2, has been extensively studied[2] in numerous cocondensation reactions. Of the volatile main-group hydrides, the reactions of SiF_2 with diborane(6),[3] germane,[4] and ammonia[2] have been reported. Solan and Burg[3] found that the cocondensation of SiF_2 and B_2H_6 yielded nonvolatile materials and diborane derivatives of the 1,1-fluorosilylated type which were thermally unstable. Germane and SiF_2 react to give products of the type $GeH_3(SiF_2)_nH$ ($n = 1–3$) and the reaction of ammonia and SiF_2 apparently yields deeply colored polymeric material.[2] To date, the cocondensation reaction of SiF_2 with silane has not been reported.

The only phosphorus-containing compounds which have been cocondensed with SiF_2 are phosphorus trifluoride and phosphorus trichloride. The reaction of SiF_2 and PF_3 was reported[5] to yield a red polymer and a mixture of unstable compounds, presumably of the type $Si_nF_{2n+1}PF_2$, which readily decomposed to perfluorosilanes and black P–F polymers. The PCl_3 reaction[6] yielded a yellow-brown polymer and volatile products containing only silicon, fluorine, and chlorine. No volatile silicon–phosphorus compounds were detected.

Although no phosphorus-containing molecules have been isolated from cocondensation reactions with SiF_2, the phosphine molecule appeared to be a potential source of volatile silicon–phosphorus compounds. Reported herein are the results of our study of the SiF_2–PH_3 cocondensation reaction.

Experimental Section

Apparatus. All work was carried out in a conventional high-vacuum system employing greaseless stopcocks. Mass spectra were obtained on a Perkin-Elmer RMU-6 spectrometer. Exact mass measurements were obtained on an AEI MS 902. Infrared spectra in the range 4000–400 cm^{-1} were recorded with a Perkin-Elmer Model 337 on gaseous samples in a 10-cm cell fitted with KBr windows. Proton and fluorine nuclear magnetic resonance spectra were obtained at 100.1 and 94.1 MHz, respectively, on a Varian Associates XL-100-15 in the CW mode. Standard variable-temperature accessories were employed. The furnace for SiF_2 preparation was built in our laboratory from Transite pipe, insulation brick, and Kanthal heating wire. Mullite tubing was used in the furnace.

Materials. Silicon tetrafluoride was obtained commercially (Matheson, 99.6% stated minimum purity) and phosphine was prepared as described in the literature.[7] Silicon difluoride was prepared as described by Timms[8] and PH_3 was introduced into the SiF_2–SiF_4 stream as close to the cocondensation trap as possible. The furnace was maintained at approximately 1300° and a SiF_4 to SiF_2 conversion of about 70% was assumed.[8]

In a typical reaction 1.9 g (56 mmol) of PH_3 and 4.7 g (45 mmol) of SiF_4 were used over a period of 3 hr. After cocondensation was complete, the apparatus was allowed to warm to room temperature under dynamic vacuum and the contents distilled into the vacuum system. After passing the reaction mixture through a −131° (*n*-pentane slush) trap to remove PH_3 and SiF_4, the remaining products were fractionated on a low-temperature vacuum distillation column.[9] The first fraction (0.3 mmol) distilled from the column in the range −125 to −120°. An infrared spectrum of this fraction exhibited the following bands: 2310 cm^{-1} (m), 2302 cm^{-1} (m), 2220 cm^{-1} (s), 1030 cm^{-1} (s), 960 cm^{-1} (vs, br), 880 cm^{-1} (vs, br), 526 cm^{-1} (m). A mass spectrum of the fraction at 70 eV exhibited the following major peaks: *m/e* 28, 31, 32, 33, 34, 47, 67, 85, 98, 99, 100, 118. At 20 eV the peaks at *m/e* 34, 100, and 118 increased significantly in intensity. A high-resolution mass spectral determination showed the peaks at *m/e* 100 and 118 to have exact masses of 99.9709 and 117.9615, respectively. The ^1H nmr spectrum of this material (−35°, 10% $CDCl_3$ solution) consisted of three resonances: a triplet of doublets (τ 4.32, J = 62.4, 24.3 Hz), a doublet of quartets (τ 8.27, J = 193.5, 4.1 Hz), and a doublet of triplets (τ 8.32, J = 191.0, 8.4 Hz). The ^{19}F nmr spectrum exhibited two resonances: a doublet of triplets (δ 47.8 ppm shielded with respect to external $C_2F_4Br_2$, J = 22.6, 4.2 Hz) and a doublet of doublets of triplets (δ 57.9 ppm shielded with respect to external $C_2F_4Br_2$, J = 61.9, 13.6, 8.3 Hz). A second fraction (~1 mmol), obtained over a wide range of temperatures, −90 to −75°, was shown by infrared, nmr, and mass spectral data to be Si_2F_5H.[10,11] Three more fractions were obtained at −55 to −60, −35 to −30, and 0 to 5°. However, the thermal instability of these fractions prevented their characterization. All three fractions decomposed when melting and when being transferred in the vacuum line. These materials were not investigated further.

Discussion

As in the reactions with the compounds PF_3[5] and PCl_3,[6] the volatile products of the cocondensation reaction of SiF_2 with PH_3 are mainly thermally unstable compounds produced in low yield. The most volatile fraction is indicated by spectroscopic measurements to consist of the new compounds difluorosilylphosphine, SiF_2HPH_2, and trifluorosilylphosphine, SiF_3PH_2. These two compounds resisted all attempts to separate them, either by trap-to-trap fractionation or by extremely slow vacuum distillation on a variable-temperature column. Thus, melting point and vapor tension determinations of these compounds were precluded. That one of these compounds is not a decomposition product of the other is shown by all spectroscopic techniques in which both compounds persist in the same relative proportions indefinitely. High-resolution mass spectral data conclusively show that both compounds are present ($^{28}Si^{19}F_2{}^{31}P^1H_3$, exptl 99.9707, calcd 99.9709; $^{28}Si^{19}F_3{}^{31}P^1H_2$, exptl 117.9619, calcd 117.9615) as do ^1H and ^{19}F nmr data.

The ^1H nmr spectrum of SiF_2HPH_2 can be assigned as follows: the more shielded multiplet at τ 8.32, assigned to the PH_2 protons, is split into a doublet by spin–spin coupling with the phosphorus atom, J_{HP} = 191.0 Hz, each line of which is further split into a triplet by coupling with the two fluorine atoms, $^3J_{HF}$ = 8.4 Hz; the less shielded multiplet at τ 4.32, assigned to the silicon hydrogen, is split into a triplet by coupling to the two fluorine atoms, $^2J_{HF}$ = 62.4 Hz, each line of which is split into a doublet by coupling with phosphorus, $^2J_{HP}$ = 24.3 Hz. Instrumental integration of the two resonances was very close to an area ratio of 2:1 after accounting for the area of the PH_2 protons of F_3SiPH_2. The relative amount of the two compounds in this sample was obtained by integration of the ^{19}F nmr spectrum. The ^{19}F nmr spectrum of SiF_2HPH_2 (a doublet of doublets of triplets) is assigned on the following basis: the doublet exhibiting the larger J value arises from coupling to the geminal proton, $^2J_{FH}$ = 61.9 Hz; the doublet of smaller J value arises from coupling with the phosphorus, $^2J_{FP}$ = 13.6 Hz; the triplet is assigned to coupling with the phosphorus protons, $^3J_{FH}$ = 8.3 Hz. The ^1H nmr spectrum of SiF_3PH_2, τ 8.27, is assigned as follows: the doublet arises from coupling with the phosphorus, J_{HP} = 193.5 Hz; the quartet arises from coupling to the three fluorines, $^3J_{HF}$ = 4.1 Hz. The ^{19}F nmr spectrum of SiF_3PH_2, δ 47.8 ppm from external $C_2F_4Br_2$, is assigned as follows: the doublet arises from coupling with the phosphorus, $^2J_{FP}$ = 22.6 Hz; the triplet arises from coupling to the two protons, $^3J_{FH}$ = 4.2 Hz. Major bands in the infrared spectrum of the SiF_2HPH_2–SiF_3PH_2 fraction can be assigned as follows: P–H stretch, 2310 and 2302 cm^{-1}; Si–H stretch, 2220 cm^{-1}; P–H_2 scissors, 1030 cm^{-1}; Si–F antisymmetric stretch, 960 cm^{-1}; Si–F symmetric stretch, 880 cm^{-1}; Si–P stretch, 526 cm^{-1}.

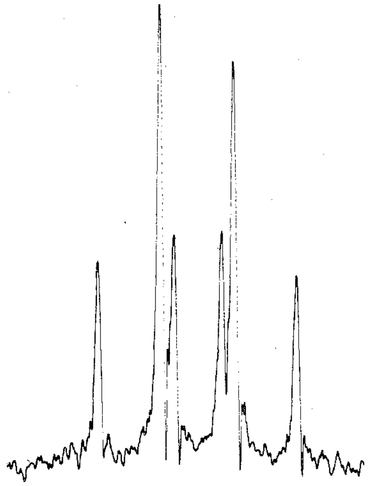

Figure 1. The SiF_3 portion of the ^{19}F nmr spectrum of Si_2F_5H showing $^3J_{FH}$ = 13.6 Hz and $^3J_{FF}$ = 11.4 Hz.

Previous cocondensation reactions of SiF_2 have shown[2] that it reacts as a diradical and gives products arising from insertion reactions. In this case SiF_2HPH_2 is thought to arise from the insertion of SiF_2 into a P–H bond of PH_3. The observation that SiF_3PH_2 is synthesized in this reaction is not surprising in view of recent work[12] by Margrave, *et al.*, who have shown that there is an appreciable concentration (10–25%) of SiF_3 in the mixture of reaction products over Si–SiF_4 at approximately 1000°.

The second product Si_2F_5H has been previously identified in the reaction of SiF_2 with H_2S[10] and with HBr.[13] In both these reactions as well as the present reaction with PH_3 the other products are unstable. This indicates that this product may be formed from decomposition of the unstable products. Another possible method of formation of this species is abstraction by the diradical SiF_2SiF_2 both of a fluorine from SiF_4 or a reaction product and a proton from PH_3 or a reaction product. Alternatively, a SiF_3 radical could react with a SiF_2 diradical to give a SiF_3SiF_2 radical which could then abstract a proton or SiF_3 could react with a SiF_2H radical.

The ^{19}F nmr spectrum of pentafluorodisilane has previously been reported[10,11] to consist of a quartet and a doublet of quartets. It was noted that the interesting feature of the spectrum was the presence of a quartet for the resonance of the SiF_3 fluorines rather than the expected doublet of triplets. This was attributed to the close similarity of the $^3J_{FH}$ and $^3J_{FF}$ values. Our ^{19}F nmr spectrum exhibited the expected doublet of triplets (see Figure 1) as well as the previously reported doublet of quartets. The coupling constant values are $^3J_{FH}$ = 13.6 Hz and $^3J_{FF}$ = 11.4 Hz. Our ^{19}F chemical shift values agreed with those previously reported.[10] There are several possible explanations why we observed the expected doublet of triplets and others have not. Trace impurities which interfere with the small splitting observed may have been shifted by the higher magnetic field strength which was used to obtain our spectra. Alternatively, improved sample purity *via* our variable-temperature vacuum fractionation column or better resolution on our instrumentation could be the difference.

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Registry No. SiF_2HPH_2, 52950-76-2; SiF_3PH_2, 51518-19-5; Si_2F_5H, 24628-33-9; PH_3, 7803-51-2; SiF_2, 13966-66-0.

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Study of Some Mixed Silyl Germyl Group VIa Derivatives

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The synthesis of GeH_3SSiH_3 and $GeH_3SSi(CH_3)_3$ has been achieved by the interaction of a 1:1 mole ratio of GeH_3Cl with $(SiH_3)_2S$ and GeH_3F with $[(CH_3)_3Si]_2S$, respectively. Germyl trimethylsilyl ether, $GeH_3OSi(CH_3)_3$, has been prepared by the interaction of $(CH_3)_3SiOLi$ with GeH_3Cl. The complete characterization of the mixed silyl germyl group VIa derivatives has not been possible owing to the tendency for the compounds to readily undergo disproportionation in the liquid phase. Infrared and ^1H nuclear magnetic resonance spectral data for the compounds are presented.

Introduction

Many of the important conclusions about the bonding characteristics of silicon and germanium have been obtained from studies of various hydride derivatives of these elements rather than from analogous organosilicon and organogermanium compounds.[1–3] Selecting the hydrides for study is especially important in cases where the organic substituents may influence the results in a significant way. Thus, in order to obtain information about the nature of the heteroatom Si–O–Ge and Si–S–Ge linkages, it would be most desirable to be able to work with the simple silyl, (SiH_3), and germyl, (GeH_3), derivatives. In this report, we present the results of research carried out to ascertain whether or not compounds of this general type could be prepared and studied.

Experimental Section

Apparatus. With the exception of the synthesis of some of the starting materials, all work was carried out in a conventional Pyrex-glass vacuum system.[4] Apparatus and techniques employed were identical with those previously described.[5]

Materials. Germyl chloride (vapor pressure at 0°: found, 236 Torr; lit.,[6] 234 Torr; purity confirmed by its infrared spectrum[7]) and GeH_3Br (mol wt: found, 155.7; calcd, 155.5; purity confirmed by its infrared spectrum[7]) were prepared by the reaction of GeH_4 with $SOCl_2$[8] and Br_2,[9] respectively. Germyl fluoride (purity confirmed by its infrared spectrum[7]) was prepared by passing GeH_3Br through a column of freshly prepared PbF_2.[10] Disilyl sulfide (vapor pressure at 0°: found, 61 Torr; lit.,[11] 61 Torr; purity confirmed by its infrared spectrum[12]) and $[(CH_3)_3Si]_2S$ (purity checked by its infrared spectrum[13]) were prepared by passing the vapors of SiH_3I and $(CH_3)_3SiI$, respectively, through a column packed with red HgS and dry sand.[11] Lithium trimethylsilanolate was prepared by reaction of CH_3Li with $[(CH_3)_3Si]_2O$.[14]

Synthesis and Identification of GeH_3SSiH_3. Germyl chloride (0.8 mmol) and $(SiH_3)_2S$ (0.8 mmol) were condensed into a 50-ml reaction vessel and allowed to stand for 5 min at room temperature. The products were distilled through traps maintained at −46, −96, and −196°. The trap at −196° contained SiH_3Cl (0.8 mmol, identification made by its infrared spectrum[15]). The trap at −46° contained a small amount of $(GeH_3)_2S$ (identification made by its infrared spectrum[16]). The infrared spectrum of the contents of the −96° trap was consistent with that expected for the mixed sulfide GeH_3SSiH_3, although the spectrum revealed the presence of a small amount of $(SiH_3)_2S$ by its characteristic Si–S symmetric stretching mode at 479 cm^{-1}. Attempts to remove the impurity were not successful and, in fact, the concentration of impurity increased after several additional purification attempts. Further studies (see below) indicated that the compound easily underwent disproportionation to form $(SiH_3)_2S$ and $(GeH_3)_2S$. Digermyl sulfide could easily be removed from the product mixture by standard fractionations, but because of their similar volatilities, $(SiH_3)_2S$ could not be removed from the GeH_3SSiH_3. The use of gas chromatography also failed to purify the mixed sulfide, even with the identical column and conditions used previously to purify GeH_3SCH_3.[17]

The formation of GeH_3SSiH_3 in the reaction was unequivocally established by the compound's characteristic proton nmr spectrum. The spectrum of a 14% by volume sample in deuteriocyclohexane (TMS added as an internal standard) consisted of two 1:3:3:1 quartets (J_{HH} = 0.8 Hz) of equal intensity centered at τ 5.59 (±0.01) (SiH_3 protons) and τ 5.41 (±0.01) (GeH_3 protons). The data are in agreement with the values obtained for this compound (prepared by an alternate route) by other workers.[18]

Synthesis of $(GeH_3)_2S$. Since it was noted in our laboratory that the purification steps in the commonly quoted synthesis of $(GeH_3)_2S$ (based on the reaction of GeH_3I with HgS) are often very tedious, we carried out a small-scale "clean" synthesis of the compound based on the reaction of pure $(SiH_3)_2S$ (1 mmol) with pure GeH_3Cl (2 mmol). The reactants were condensed into a 50-ml tube and allowed to react for 5 min. Pure $(GeH_3)_2S$ (1.0 mmol) was isolated from the products in a −45° trap in one standard vacuum-line distillation from room temperature to −45° to −196°. The purity of the material was confirmed by its infrared spectrum[16] and by its vapor pressure at 0° (5.0 Torr, lit.[16] value 5.0 Torr).

Synthesis and Identification of $GeH_3SSi(CH_3)_3$. Germyl fluoride (0.8 mmol) and $[(CH_3)_3Si]_2S$ (0.8 mmol) were condensed into a 50-ml reaction vessel and allowed to stand for 5 min at room temperature. The products were distilled through traps maintained at −83 and −196°. An infrared analysis of the two fractions indicated that the trap at −196° contained mostly $(CH_3)_3SiF$[19] with some GeH_3F[7] and a trace of GeH_4,[20] while the trap at −83° contained $[(CH_3)_3Si]_2S$,[13] $(GeH_3)_2S$,[16] and the mixed sulfide $GeH_3SSi(CH_3)_3$. Absorptions in the nmr spectrum of the sample (14% by volume in deuteriocyclohexane with C_6H_{12} added as an internal standard) confirmed the presence of $[(CH_3)_3Si]_2S$ (τ 9.67) and $(GeH_3)_2S$ (τ 5.38).[17,21]