plot between the pK_a's of several substituted pyridines and the Hammett σ constant.

A number of investigators have studied the relationship between the basicity of pyridines and their ability to form various types of complexes. A comprehensive study of the relationship between the pK_f values of silver complexes of amines with their pK_a values by Bruehlman and Verhoek[18] has shown that plots of pK_f *vs.* pK_a fall on two straight lines, one for the pyridines and primary aliphatic amines and one for secondary amines. Recently Cattalini and coworkers[19] have shown that the plot of log K for the reaction $AuCl_4^- + py \rightleftarrows Au(py)Cl_3 + Cl^-$ gave three straight lines, one for pyridines without steric hindrance, one for pyridines with one methyl group in the 2 position, and a third one for pyridines with methyl groups in the 2 and 6 positions.

It can be concluded, therefore, that in pyridine and in substituted pyridines, in the absence of steric effects, there is a definite parallelism between the complexing abilities of the amines and their basicities. Such correlation, of course, would be expected if one adopts Lewis' definition of acids and bases since both H^+ and I_2 are Lewis acids. It should be noted, however, that such generalizations are only applicable to cases where the reference bases do not differ appreciably in structure.

Acknowledgment.—The authors gratefully acknowledge the support of this work by the U. S. Army Research Office (Durham).

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[18] R. J. Bruehlman and F. H. Verhoek, *J. Am. Chem. Soc.*, **70**, 1401 (1948).

[19] L. Cattalini, M. Nicolini, and A. Orio, *Inorg. Chem.*, **5**, 1674 (1966).

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF MICHIGAN, ANN ARBOR, MICHIGAN 48104

Fluorophosphine Ligands. V. Reactions of μ-Oxo-bis(difluorophosphine), F_2POPF_2, with Acids

BY L. F. CENTOFANTI AND R. W. PARRY

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The compound F_2POPF_2 adds one and only one BH_3 group when brought into contact with B_2H_6 at a pressure of 1 atm and a temperature of 25°. Dissociation of $F_2POPF_2\cdot BH_3$ is favored by higher temperatures and reduced pressures; the immediate products are F_2POPF_2 and B_2H_6. Analyses of the ^{19}F, ^{11}B, and ^1H nmr spectra prove that the BH_3 is bound to one of the phosphorus atoms. No reaction is observed with BF_3 and F_2POPF_2. The addition of HBr to F_2POPF_2 leads to the cleaving of the P–O–P bond with the formation of F_2HPO and PF_2Br. The structure of F_2HPO has been established by means of the ^{31}P, ^{19}F, and ^1H nmr spectra. The compound F_2HPO has also been observed in the reaction of PF_3 with small amounts of H_2O at 150° and in the reaction of $(CH_3)_3SnOH$ with PF_2Br. When F_2HPO is maintained as a liquid at room temperature, disproportionation to give PF_3 and the previously unreported $FHPO_2H$ occurs. The ^{31}P, ^1H, and ^{19}F nmr spectra were used to identify monofluorophosphorous acid, $FHPO_2H$.

The recently reported[1] compound F_2POPF_2 has three potentially basic sites; hence, a number of possible reactions with acids might be anticipated. Transformations resulting from reactions with both Brønsted and Lewis acids are described herein.

The Reaction of F_2POPF_2 with Lewis Acids

(1) **With Diborane.** Diborane reacts with F_2POPF_2 as indicated by the equation

$$\tfrac{1}{2}B_2H_6(g) + F_2POPF_2(g) \xrightarrow{25°} F_2POPF_2\cdot BH_3(g)$$

Yields of 85% were obtained. No evidence for a double or triple adduct was obtained under the conditions used here. The boron-11 nmr spectrum of $F_2POPF_2\cdot BH_3$ was obtained at 32.1 Mc using a Varian HR-100; the expected borane quartet was observed. (J_{BH} = 104 cps; δ relative to $B(CH_3)_3$ = 130 ppm). Each member of the quartet was split into a doublet by direct coupling with phosphorus (J_{BP} = 55.8 cps). The B–P coupling constant of 55.8 is comparable to the value of J_{BP} (54.3 cps) in $(CH_3)_2HPBH_3$ where direct B–P bonding is mandatory. Thus, bonding of a BH_3 unit to one of the phosphorus atoms is clearly indicated. Boron–phosphorus coupling in $F_2POPF_2\cdot BH_3$ contrasts sharply with a lack of such coupling in $F_2PPF_2\cdot BH_3$. A rapid intramolecular exchange of BH_3 between P atoms was postulated to explain the lack of coupling in $F_2PPF_2BH_3$.[2] Such rapid exchange between coordination sites is definitely not taking place in $F_2POPF_2BH_3$.

The phosphorus-31 nmr spectrum was obtained at 40.4 Mc on a Varian HR-100 spectrometer. The spectrum confirms the fact that a borane group is directly bonded to only one of the two phosphorus atoms. Three sets of triplets were observed; the first was that for the free F_2POPF_2 in the system[3] (δ relative to

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[1] R. W. Rudolph, R. C. Taylor, and R. W. Parry, *J. Am. Chem. Soc.*, **88**, 3729 (1966).

[2] K. W. Morse and R. W. Parry, *ibid.*, **89**, 172 (1967).

[3] Some difficulty was experienced in separating small amounts of F_2POPF_2 from $F_2POPF_2\cdot BH_3$. Slow decomposition to give F_2POPF_2 and B_2H_6 at reduced pressures and low temperatures would explain the observation. Thermodynamic quantities for the system F_2POPF_2–B_2H_6 are being obtained.

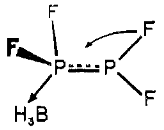
H_3PO_4 = −111 ppm, J_{PF} = 1354 cps). The second set of triplets corresponded to the uncomplexed F_2P– group in the molecule (δ = −105.5 ppm (H_3PO_4), J_{PF} = 1386 cps). Each member of this triplet was split into a doublet through coupling to phosphorus, J_{POP} = 26.7 cps. The third triplet (δ = −100.7 ppm, J_{PF} = 1328 cps) corresponded to the phosphorus in the $-PF_2 \cdot BH_3$ moiety. Because of additional splitting of this signal by boron, phosphorus, and hydrogen, as well as boron quadrupole broadening, individual members of this triplet could not be further resolved.

Proton spectra were obtained on a Varian HA-60 and a Varian HR-100A. The tracing showed the expected 1:1:1:1 quartet (J_{BH} = 104 cps, δ relative to TMS = 1.56 ppm); each member of the quartet was split into a doublet (J_{PBH} = 17 cps) and each doublet was then split into a triplet (J_{FPBH} = 17 cps). Because the P–B–H and F–P–B–H coupling constants are equal, the patterns overlapped giving a broad 1:3:3:1 quartet for each member of the original quartet. Independent confirmation of the value of 17 cps for J_{FPBH} was obtained from the fluorine spectrum, while the value of 17 cps for J_{PBH} is identical with that found by Rudolph in the related compound F_2HPBH_3.[4] Similarly in F_3PBH_3, J_{FPBH} and J_{PBH} both have the value of 18 cps.[4]

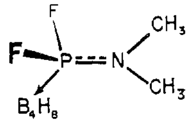
The fluorine spectrum of $F_2POPF_2BH_3$, obtained at 94.1 Mc, shows the expected three sets of doublets. The first set corresponds to the uncomplexed or free F_2POPF_2 (confirmed by ^{31}P spectrum); the previously reported[1] fine structure was apparent on further resolution. The free F_2P– unit in the complexed F_2POPF_2 gave a clear doublet (J_{PF} = 1387 cps, δ relative to TFA = −41.5 ppm) and the $-F_2PBH_3$ unit gave a doublet (J_{PF} = 1328 cps, δ = −24.5 ppm) each member of which was split by the three B–H hydrogens into a 1:3:3:1 quartet (J_{HBPF} = 17 cps).

(2) **With Boron Trifluoride.**—All attempts to prepare $F_2POPF_2 \cdot BF_3$ using techniques comparable to those used successfully in the preparation of $F_2POPF_2 \cdot BH_3$ gave only unaltered starting materials.

The Properties of Lewis Acid Adducts of F_2POPF_2 and F_2PPF_2. A Discussion.—The base F_2POPF_2 resembles F_2PPF_2 in that only *one* basic site will pick up a BH_3 unit under the mild conditions used here. In the case of $F_2PPF_2 \cdot BH_3$, reduced base strength of the second phosphorus was attributed to a possible transfer of electrons from one phosphorus to the other through the P–P π system. Further, the proximity of the two coordination sites made exchange of the BH_3 group between sites possible. Even a P–B–P bridge interaction could not be excluded for $F_2PPF_2 \cdot BH_3$. As a result of the proximity of $-PF_2$ units and the perturbing power of the coordinating borane, $F_2P–PF_2 \cdot BH_3$ underwent decomposition to give F_3PBH_3 and $[P–F]_n$ rather than P_2F_4 and BH_3. An intermediate of the general form



might be suggested by analogy to the known structure[5] of $F_2PNR_2 \cdot B_4H_8$



In such an intermediate, easy shifting of a fluorine as indicated by the arrow would give the observed F_3PBH_3 and PF. Polymerization of PF units would then give the observed $[PF]_n$. In contrast, the interposing of an oxygen atom between PF_2 units to give F_2POPF_2 appears to prevent borane group exchange and effectively blocks fluorine transfer. As a consequence, a prime mode of decomposition of $F_2POPF_2BH_3$ is dissociation to give F_2POPF_2 and B_2H_6.

Electron distribution in $F_2POPF_2BH_3$ poses a more difficult problem. In certain molecular conformations, orbital symmetry would permit some electron interchange between PF_2 units by way of the π system of the oxygen. Electron drift toward the coordinated PF_2 unit would enhance the base strength of that phosphorus and reduce the base strength of the noncoordinated $-PF_2$. Coordination of only a single BH_3 could thus be rationalized. All of the above postulates are consistent with current information.

In addition to the relatively rapid decomposition of $F_2POPF_2BH_3$ to give the starting materials, a secondary, slow, and more complex process was observed when $F_2POPF_2BH_3$ was allowed to stand in a sealed tube at 25° for 1 month. Approximately 0.5 mole of H_2 was liberated for each mole of $F_2POPF_2BH_3$ undergoing reaction, and a clear yellow solid remained as a product. The process is being studied further.

It is of interest to note that F_2POPF_2, like PF_3, will not form an adduct with BF_3. We attribute this to a high deformation energy which is required to convert planar BF_3 to tetrahedral $BF_3 \cdot L$. If the deformation energy exceeds the low bonding energy, no adduct forms. Since BH_3 has a much lower deformation energy, it will coordinate with weakly basic ligands.

Reactions of F_2POPF_2 with Brønsted–Lowry Acids

(1) **The Reaction of F_2POPF_2 with HBr. The Synthesis of F_2HPO.**—When HBr and F_2POPF_2 are mixed in the gas phase at 25°, the P–O–P bond is cleaved. The equation for the process is

$$F_2POPF_2(g) + HBr(g) \longrightarrow F_2HPO(g) + F_2PBr(g)$$

The F_2HPO, obtained in 85% yield, is identical with the F_2HPO first reported by Treichel, Goodrich, and Pierce[6] as a by-product in the decomposition of HPF_4.

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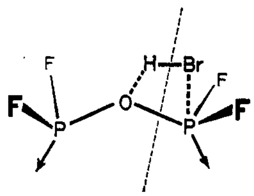
[4] R. W. Rudolph and R. W. Parry, *J. Am. Chem. Soc.*, **89**, 1621 (1967).

[5] R. M. Douglas and C. E. Nordman, submitted for publication. The $P{-}N{<}^{C}_{C}$ unit is almost planar and bisects the FPF angle.

[6] P. M. Treichel, R. A. Goodrich, and S. B. Pierce, *J. Am. Chem. Soc.*, **89**, 2017 (1967).

The products obtained in the HBr–F_2POPF_2 reaction suggest possible initial attack of the proton on the oxygen rather than the phosphorus. A four-center intermediate would be expected as bromine attacks the phosphorus



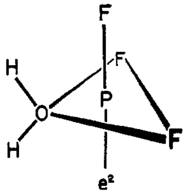
Rupture of the POP bond along the dashed line would give F_2PBr and F_2POH. An expected rapid rearrangement of F_2POH would give F_2HPO. Since the reaction proceeds readily even at −78°, it was not possible to obtain the nmr spectrum of the proposed intermediate $F_2POPF_2 \cdot HBr$.

(2) **Other Syntheses of F_2HPO. The Rearrangement of F_2POH.**—When a sample of PF_3 (3.24 mmoles) was allowed to react with a deficiency of water vapor (0.360 mmole) for 2 days at 150° in a sealed 100-cc reaction tube, F_2HPO (0.127 mmole) could be separated from the products in a trap held at −95°. A second trap held at −196° retained PF_3 and SiF_4. SiF_4 resulted from the action of HF on the glass. The process can be represented by the equation

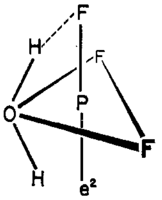
$$F_3P(g)\ (\text{excess}) + H_2O(g) \xrightarrow[2\ \text{days}]{150°} F_2HPO(g) + HF(g)$$

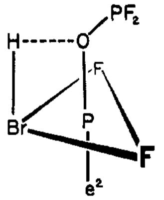
Other reactions, not identified, left a clear oil and a yellow solid in the reaction tube. When equal amounts of H_2O and PF_3 were used, any F_2HPO formed was rapidly destroyed by the water present.

The following reaction scheme is consistent with the known products as well as with the known chemistry of PF_3. The first gas phase intermediate is visualized as an addition compound, $F_3P \cdot H_2O$. Precedent for this compound is available, since it is known that PF_3 serves as a Lewis acid toward $N(CH_3)_3$[7] to give $F_3P \cdot N(CH_3)_3$. Loss of HF from this intermediate would give F_2POH which, as in the preceding case, would rearrange rapidly to give F_2HPO.



The initial four-center intermediates suggested for the H_2O–PF_3 reaction and for the HBr–F_2POPF_2 reaction are not vastly different





The ready rearrangement of F_2POH to F_2HPO is of interest since Griffiths and Burg[8] found that the closely related compound $(CF_3)_2POH$ does not rearrange. In fact, the rearrangement seems to proceed in the opposite direction. They attributed their observation to a withdrawal of electrons from the phosphorus by the strongly electronegative $-CF_3$ groups. As electrons are withdrawn from the phosphorus, the bonding power of the phosphorus lone pair is reduced to the point that the proton will not bind to the phosphorus directly. In general, fluorine atoms are considered to be as electronegative as $-CF_3$ groups. In view of the new facts now available, one must accept one of the following conclusions: (a) the $-CF_3$ group is more electronegative than −F, (b) the electron-withdrawing power of the group on the phosphorus is not germane to the rearrangement, or (c) F_2HPO is stabilized by an effect not present in $(CF_3)_2HPO$. (Possible items such as fluorine π bonding, steric interference, etc., might be advanced.)

The rapid rearrangement of F_2POH suggests that F_2HPO might be synthesized from F_2PX compounds (where X = Cl, Br, or I) by replacing X with an OH group. Such replacement can be carried out using $(CH_3)_3SnOH$. A typical reaction is

$$\begin{tikzcd}[column sep=small] F_2PCl(g) + (CH_3)_3SnOH(l) \arrow[r] & F_2POH(g) \arrow[d] & + (CH_3)_3SnCl \\ & F_2HPO & \end{tikzcd}$$

The Properties of F_2HPO

(1) **The Nmr Spectra.**—The ^{31}P spectrum of F_2HPO consisted of a triplet, each member of which was split into a doublet; the ^{19}F spectrum consisted of a doublet, each member of which was further split into a doublet; the proton spectrum showed a doublet, each member of which was further split into a triplet. The coupling constants and chemical shift values are given in Table I. The spectra provide conclusive evidence for the compound.

TABLE I

NMR DATA FOR F_2HPO

	From ^{31}P spectrum	From ^1H spectrum	From ^{19}F spectrum
J_{P-H}, cps	881	878	
J_{P-F}, cps	1112		1114
J_{H-F}, cps		116	114
δ_P (OPA), ppm	+1		
δ_F (TFA), ppm			−13.5
δ_H (TMS), ppm		−7.02	

(2) **The Boiling Point of F_2HPO and Spectral Shifts.**—The boiling point of F_2HPO (67.7°) is very high when compared to that of F_3PO (−39.8°). A large amount of molecular interaction such as hydrogen bonding of the form P–H---F—P or P–H---O—P is implied by these differences in volatility. On the other hand the

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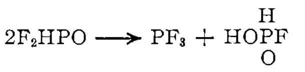
[7] (a) R. R. Holmes and R. P. Wagner, *Inorg. Chem.*, **2**, 384 (1963); (b) an unequivocal decision as to whether the electron pair in F_3POH_2 should be axial or equatorial is clouded by conflicting arguments and no data are available. This structural detail is of no immediate concern to the mechanistic arguments used.

[8] J. E. Griffiths and A. B. Burg, *J. Am. Chem. Soc.*, **82**, 1507 (1960).

infrared spectral shifts between gaseous and liquid phases are not those usually expected for hydrogen bonding. For example, the P–H stretching frequency appears at 2503.1 cm^{-1} in the gas phase but at a *higher* frequency, 2570.8 cm^{-1}, in the solid phase. Usually the X–H stretching frequency is lowered by hydrogen bonding. The unexpected shift of P–H to higher frequencies on going from gas to solid is exactly analogous to the shift found in the related compound F_2HP.[9] The P=O stretching frequency *drops* from 1380 cm^{-1} in the gas phase to 1310 cm^{-1} in the solid phase. Although this shift is in the right direction, it cannot be attributed to hydrogen bonding in F_2HPO, since a comparable shift is observed in F_3PO on going from gas (1415 cm^{-1}) to solid (1385 cm^{-1}). In the latter case no hydrogen bonding is possible. The details of the spectrum of F_2HPO are still to be resolved.

(3) Chemical Properties of F_2HPO. The Synthesis of Monofluorophosphorous Acid.—As a gas in a well-dried ir cell, F_2HPO has been kept for several hours with no noticeable decomposition. In the presence of 91 mole % PF_3 (total pressure 1 atm), it is stable in the gas phase for at least 2 days at 150° with no detectable decomposition.

On the other hand, liquid F_2HPO undergoes complete reaction over a 5-hr period at 25°. The equation for the process is



$$2F_2HPO \longrightarrow PF_3 + HO\overset{H}{\underset{O}{P}}F$$

The resulting monofluorophosphorous acid, which has not been reported previously, was characterized by means of ^{19}F, ^{1}H, and ^{31}P nmr data. The ^{31}P spectrum of HFPO(OH) was a doublet of doublets as was the ^{19}F spectrum. The ^{1}H spectrum was a doublet of doublets and a singlet; the area in the ^{1}H spectrum under the doublets was equal to that under the singlet. The coupling constants and chemical shift data are summarized in Table II.

Table II

Nmr Data for H_2PO_2F[a]

	^{31}P	^{1}H	^{19}F
J_{P-H}, cps	784	782	
J_{P-F}, cps	1028		1030
J_{H-P-F}, cps		114	114
δ_P (OPA), ppm	−2.74		
δ_F (TFA), ppm			−15.6
δ_{PH} (TMS), ppm		−7.92	
δ_{OH} (TMS), ppm		−14.2	

[a] OPA, orthophosphoric acid; TFA, trifluoroacetic acid; TMS, tetramethylsilane.

Since disproportionation of F_2HPO to give FHPO(OH) seems to occur more easily in the liquid phase than in the gas phase, association of molecules in the liquid state (perhaps through hydrogen bonding) may well initiate the disproportionation process.

Experimental Section

Standard high-vacuum techniques were employed. Diborane was kindly supplied by Callery Chemical Co. (Callery, Pa.). Trifluorophosphine was obtained from the Ozark Mahoning Co.; BF_3 and HBr were obtained from the Matheson Co.; μ-oxo-bis-(difluorophosphine) was prepared from the reaction of PF_2I and Cu_2O.[1] Trimethyltin hydroxide was obtained from Alfa Inorganics, Inc.

Synthesis of $F_2POPF_2BH_3$.—A 0.685-mmole sample of F_2POPF_2 and a 1.21-mmole sample of B_2H_6 were added to a 50-ml reaction tube. After standing overnight at 25°, the mixture was distilled through traps at −78, −112, and −196°. A sample of $F_2POPF_2 \cdot BH_3$ amounting to 0.585 mmole was found at −112°. The molecular weight of a freshly purified sample was determined by vapor density at 23.7° and 70 mm: calcd for $F_2POPF_2BH_3$, 167.8; found, 167.6.

Syntheses of F_2HPO. (a) By the Reaction of HBr and F_2POPF_2.—A 5.77-mmole sample of HBr was frozen into a 500-ml bulb containing 5.81 mmoles of F_2POPF_2. After standing for 0.5 hr at room temperature, the mixture was distilled through traps held at −45, −95, and −196°. A 4.92-mmole sample of F_2HPO was found in the −95° trap (yield 85% based on HBr). The −196° trap contained F_2PBr, F_2POPF_2, and HBr. The molecular weight was determined at 21.5° and 76.5 mm by vapor density: calcd for F_2HPO, 86.0; found, 87.3. The mass spectrum shown in Table III is consistent with the structure assigned from nmr, but relative peak heights differ somewhat from those obtained by Treichel, *et al.*[6]

Table III

Mass Spectrum of F_2HPO (Ionization Voltage 70 V)[a]

m/e	Possible assignment	Intens rel to F_2HPO^+
15.5	P^{2+}	1.45
16	O^+	4.97
19	F^+	3.58
20	HF^+	5.74
23.5	PO^{2+}	1.36
25	PF^{2+}	1.64
31	P^+	13.4
32	PH^+	2.24
41	PO^+	67.60
50	PF^+	14.04
51	HPF^+	1.47
66	OPF^+	47.16
67	$OPFH^+$	43.08
69	PF_2^+	71.4
85	OPF_2^+	29.24
86	OPF_2H^+	100

[a] Obtained on a Consolidated Electrodynamics Model 21-103B mass spectrometer.

(b) By the Reaction of R_3SnOH and PF_2X (R = Alkyl; X = I, Br, Cl).—A 1.002-g (5.74-mmole) sample of $(CH_3)_3SnOH$ was placed in a 100-ml reaction tube. A 6.11-mmole sample of PF_2I was condensed into the tube and allowed to warm to room temperature. After the reaction had ceased, the products were distilled through traps held at −45, −78, and −196°. The −78° trap contained 0.291 mmole of F_2HPO. Somewhat better results were obtained with PF_2Br and PF_2Cl.

The Decomposition of F_2HPO.—A 10.92-mmole sample of F_2HPO was added to a thin-walled nmr tube. After about 5 hr the ^{31}P, ^{1}H, and ^{19}F spectra for F_2HPO had been replaced by spectra for PF_3 and HOPHFO. (See earlier discussion.) The nmr tube was opened and the products were led through traps at −35.6, −78, and −196°. The −196° trap contained 5.65 mmoles of PF_3 and the −78° trap contained a little unreacted F_2HPO. HOPHFO stopped at −35.6° but was difficult to separate from the last traces of HF_2PO.

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[9] R. W. Rudolph and R. W. Parry, *Inorg. Chem.*, **4**, 1341 (1965).

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Contribution from the Department of Chemistry,
San Diego State College, San Diego, California 92115

The Formation and Cleavage of the Germanium–Germanium Bond in Digermane

By W. R. BORNHORST and M. A. RING

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Digermane was prepared from the reaction between potassium germyl and chlorogermane. Catalyzed decompositions of digermane going to germane were examined with lithium chloride, bromide, and hydride. The reaction of either digermane or germane with potassium hydride produced potassium germyl. The results from these reactions and similar reactions with disilanes are discussed.

Introduction

Alkali metal salt catalyzed disproportionation reactions of disilane have recently been described.[1] Since germanium lies directly below silicon in the periodic table, it should be of interest to examine similar reactions for digermane.

At this time, the best synthesis for digermane appears to be the passing of germane through an electric discharge.[2] Since coupling reactions have been successful for the preparation of disilane[3] and germylsilane,[4] we have also examined the coupling reaction between potassium germyl and chlorogermane.

Experimental Section

The cleavage and coupling reactions were carried out in 100-ml round-bottom flasks which were fitted with either Teflon needle valves or stopcocks and ground joints to allow for transfer of volatile compounds between the vacuum line and the reaction vessels. The reaction vessels were also fitted with a side tube through which solids could be added. Infrared spectra were obtained in 5- or 10-cm gas cells, fitted with sodium chloride or potassium bromide windows using a Perkin-Elmer Model 337 spectrophotometer. The proton nmr spectrum was obtained on a Varian Model A-60 spectrometer.

Germane was prepared by the reduction of germanium oxide[2] and purified by passage through a −130° trap. The germane was identified by a vapor pressure of 40 torr at −131°, lit.[5] value 40 torr, and confirmed by an infrared spectrum[6] in which the very strong 755-cm^{-1} absorption of digermane[7] was absent. Chlorogermane was prepared from the reaction of germane with silver chloride[8] and identified by a high pressure (∼300 torr) infrared spectrum[9] which demonstrated that hydrogen chloride was absent and also from a proton nmr spectrum which had only one absorption at τ 4.86, lit.[10] value τ 4.89.

Potassium hydride (50% slurry in Bayol 85), lithium hydride, lithium deuteride, hydrogen chloride, silver chloride, and germanium dioxide were obtained commercially and were used without purification.

The 1,2-dimethoxyethane (bp 83–85°) was mixed with a large amount of potassium sand in an evacuated flask equipped with a stopcock. The flask was stored in a −78° bath when not in use to maintain the deep blue color.

The lithium halides were stored for approximately 12 hr in a vacuum oven at 125° prior to use. After transfer to the reaction vessel, the lithium halides were heated again for 1 hr under dynamic vacuum.

Potassium germyl was prepared by the method reported by Kennedy, *et al.*, for potassium silyl.[3] Excess potassium sand was treated with germane in 1,2-dimethoxyethane at −78° until the solution turned blue (2–40 hr) at which time the solvent was distilled from the reaction vessel. Treatment of the potassium germyl with hydrogen chloride yielded germane and digermane in 80 and 15% yields, respectively, based on the germane consumed in the preparation of potassium germyl. The excess potassium sand was present during the reaction with hydrogen chloride.

1. **Preparation of Digermane.**—(a) Potassium germyl (∼2.5 mmol) prepared in 1,2-dimethoxyethane as described above was filtered to remove the excess potassium. The solvent was removed by distillation until the salt was just free flowing. Chlorogermane (2.46 mmol) was condensed onto the potassium germyl. After 12 hr at room temperature, the volatile components were distilled into the vacuum system for separation. The condensate in the −196° trap was germane (0.55 mmol) identified as previously described. The condensate in the −130° trap was digermane and chlorogermane, and the condensate in the −95° trap was chlorogermane. The similarity in the vapor pressures of digermane and chlorogermane made it expedient to destroy the chlorogermane by a hydrolysis reaction with water for 2 hr. Digermane is unaffected by contact with water for 24 hr. The digermane isolated (0.45 mmol) after treatment with water and distillation through a trap cooled to −95° was identified by an infrared spectrum[17] in which the strong 431-cm^{-1} band of chlorogermane and the strong 819-cm^{-1} band of germane were absent. The vapor pressure of the digermane was 0 at −130° (no germane) and 3 torr at −78°; lit.[5] value 3 torr. The quantity of chlorogermane initially condensed in the −95° trap and retained in the water was 1.5 mmol.

(b) Chlorogermane (2.46 mmol) was condensed onto potassium

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