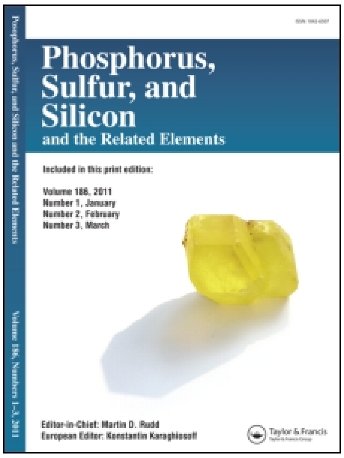

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REDISTRIBUTION OF PRIMARY SILYL- AND GERMYLPHOSPHINES: SYNTHESIS OF TRISILYL- AND TRIGERMYLPHOSPHINES

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Redistribution reactions of SiH_3PH_2, $Si_2H_5PH_2$, $SiH_3PH_2/Si_2H_5PH_2$, and GeH_3PH_2 promoted by $BX_3(X = F, Cl, Br)$, B_2H_6, and B_5H_9 as routes to the trisilyl- and trigermylphosphines $(SiH_3)_3P$, $(Si_2H_5)_3P$, $(SiH_3)_2PSi_2H_5$, and $(GeH_3)_3P$ have been examined. Reaction of the silyl- or germylphosphine borane complex (e.g. $SiH_3PH_2 \cdot BF_3$) with the uncomplexed silyl- or germylphosphine (e.g. SiH_3PH_2) appears essential to the redistribution process. Trisilylphosphines and $(GeH_3)_3P$ are best obtained in $RPH_2(R = SiH_3, Si_2H_5)$—$BF_3$ and GeH_3PH_2—B_5H_9 reaction systems, respectively.

INTRODUCTION

Unsubstituted trisilyl- and trigermylphosphines, such as $(SiH_3)_3P$ and $(GeH_3)_3P$, offer potential as reagents for the synthesis of complex metal phosphides[1] and silicon, germanium or phosphorus structural and/or electronic materials.[2] They could be especially valuable for the latter because they might provide routes to high purity, carbon-free products.

Of the trisilyl- and trigermylphosphine formation reactions reported: for $(SiH_3)_3P$, KPH_2/SiH_3X (X = halogen)[3] or SiH_3I/P_4^4 reactions and SiH_3PH_2 redistribution;[5–7] for $(Si_2H_5)_3P$, $Si_2H_5PH_2$ redistribution;[5,8] and for $(GeH_3)_3P$, GeH_3PH_2 disproportionation[9] and $GeH_3Br\text{-}(SiH_3)_3P$ exchange,[10] the redistribution reactions

$$3{\geqslant}\text{E-PH}_2 \rightarrow 2PH_3 + ({\geqslant}E)_3P \qquad (1)$$
$$(E = Si \text{ or } Ge)$$

offer greatest potential for general synthesis. In addition, they use easily available and purified primary silyl- and germylphosphine[11,12] starting materials and can yield the products in reaction mixtures from which they are easily separated.

Although borane (BX_3 = H, F, Cl, Br) promoted redistribution reactions are described,[5–8] the reports are sufficiently incomplete that their application to general trisilyl- and trigermylphosphine synthesis has not been established. In particular, the role of competing silyl- or germylphosphine-borane adduct formation (Equation 2)

$${\geqslant}\text{E-PH}_2 + BX_3 \rightarrow {\geqslant}\text{E-PH}_2 \cdot BX_3 \qquad (2)$$

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and acid cleavage of Si–P or Ge–P bonds (Equation 3) is not clear.[5–8,13,14]

$$\geqslant E\text{-}PH_2\cdot BX_3 \rightarrow \geqslant E\text{-}X + 1/x(H_2PBX_2)_x \qquad (3)$$

We have recently investigated borane-promoted SiH_3PH_2, $Si_2H_5PH_2$, $SiH_3PH_2/Si_2H_5PH_2$, and GeH_3PH_2 redistribution reactions in detail in order to obtain answers to these questions. Our results are reported below.

EXPERIMENTAL

Apparatus and Materials. All volatile materials were handled in a standard high-vacuum system.[15] Reaction mixtures were separated using a low-temperature fractional distillation column.[15] Proton nmr data were obtained at 60.0 and 100.0 MHz using Varian A-60A and HA-100 spectrometers, respectively. Phosphorus-31 nmr data were obtained at 40.5 MHz using Varian HA-100 and JEOL FX-90Q spectrometers. Chemical shifts (+δ down field) were measured relative to internal $(CH_3)_4Si(^1H)$ and 85% $H_3PO_4(^{31}P)$. IR spectra were obtained using Perkin-Elmer Models 21 and 137B (4000–400 cm^{-1}) spectrometers on gaseous samples in 10-cm cells equipped with KBr windows. Mass spectra were measured at 70 eV with a Varian MAT CH-5 spectrometer. Inlet systems and sample chambers were predried with SiH_3PH_2.

Monosilylphosphine (SiH_3PH_2),[11,16] $Si_2H_5PH_2$,[11] GeH_4,[17] GeH_3PH_2,[12] Si_2H_6,[18] and B_2H_6[19] were prepared as described previously. Boron trifluoride (Matheson Co.), BCl_3 (Matheson Co.), BBr_3 (Alfa Inorganics), and B_5H_9 (Callery Chemical Co.) were purified by fractional distillation before use. Trisilylphosphine was prepared by the method of Boeters[3] and the BF_3-promoted redistribution of SiH_3PH_2 described in this paper. Deuterium oxide (Bio-Rad Laboratories) was used as obtained. The SiH_3PD_2 was obtained from the controlled deuterolysis of $(SiH_3)_3P$.

General Reactions. Typically, the silyl- or germylphosphine and borane or boron trihalide were condensed at −196°C into a 10-50 mL reaction vessel equipped with a Fischer–Porter greaseless valve. Representative reactions for situations where trisilyl- and trigermylphosphine products were produced are summarized in Table I. After the reactions occurred at the temperatures and times indicated,

TABLE I

Redistribution reaction syntheses of trisilyl- and trigermylphosphines

Reactants (mmol)	Time (hr),	Temp. (°C)	Volatile reaction Materials (mmol)
SiH_3PH_2 (1.91) BF_3 (5.30)	10,	−78	PH_3 (1.23), BF_3 (5.23), SiH_3F (0.11), $(SiH_3)_2PH$ (0.04), $(SiH_3)_3P$ (0.53)
SiH_3PH_2 (0.29) BF_3 0.045)	10.5,	−78	BF_3 (0.033), SiH_3F (0.02), PH_3 (0.08), SiH_3PH_2 (0.16), $(SiH_3)_2PH$ (0.22),$(SiH_3)_3P$ (0.03)
SiH_3PH_2 (0.89) BCl_3 (0.34)	43, 1,	−78 −45	PH_3 (0.02), SiH_3PH_2 (0.17), $(SiH_3)_2PH/$ $(SiH_3)_3P$ (0.01), SiH_3Cl (0.64)
$Si_2H_5PH_2$ (3.42) BF_3 (10.5)	9, 4,	 −78 −45	PH_3 (2.28), SiH_3F (0.21), BF_3 (10.3), Si_2H_6 (0.21), $(Si_2H_5)_2PH$ (0.40), $(Si_2H_5)_3P$ (1.03)
$Si_2H_5PH_2$ (3.44) SiH_3PH_2 (10.6) BF_3 (47.5)	18, 7,	−78 −78	BF_3 (47.1), SiH_3F (0.53), PH_3 (9.35), Si_2H_6 (0.21), $(SiH_3)_3P$ (2.1), $(SiH_3)_2PSi_2H_5$ (1.75),[a]
GeH_3PH_2 (0.54) BF_3 (5.85)	4.6,	−112	PH_3/BF_3 (5.25), GeH_3F (0.15), $(GeH_3)P$ (0.10)
GeH_3PH_2 (0.57) B_2H_6 (2.50)	6.3, 4.0,	−112 −45	PH_3/B_2H_6 (2.08), GeH_4 (0.03) $(GeH_3)P$ (0.15)
GeH_3PH_2 (0.82) B_5H_9 (2.50)	0.2,	−45	PH_3 (0.55), B_5H_9 (2.44),[b] $(GeH_3)_3P$ (0.23)

[a] Lowest volatility fraction, presumed to be a $SiH_3P(Si_2H_5)_2/(Si_2H_5)_3P$ mixture was not measured.

[b] Fraction contained a trace of GeH_3PH_2.

the reaction materials were isolated. These materials, [PH_3,[20,21] SiH_3F,[22] SiH_3Cl,[22] SiH_2Cl_2,[23] SiH_3Br,[24] Si_2H_6,[25] $(SiH_3)_3PH$,[26] $(SiH_3)_3P$,[27,28] $(SiH_3)_2PSi_2H_5$,[29] $(Si_2H_5)_3P$,[8] and $(GeH_3)_3P$[9,10]] were characterized by comparison of their spectral (IR, ^1H and ^{31}P nmr, and mass) properties and vapor tension data with literature values.

(A) *SiH_3PH_2/BF_3.* Reaction materials (Table I), removed from the reactor at −78°C, were passed through a −130°C trap into a −196°C trap. The PH_3, BF_3, SiH_3F mixture (−196°C trap) was separated by successive removal of BF_3 and SiH_3F by their complexation with $(C_2H_5)_2O$ and $(CH_3)_3N$, respectively. Products which remained in the reactor at −78°C, $(SiH_3)_2PH$ and $(SiH_3)_3P$, were removed and separated by low-temperature fractional distillation. Traces of uncharacterized nonvolatile solid remained in the reaction vessel after removal of volatile products.

In two separate experiments, BF_3-promoted redistribution of SiH_3PH_2 (0.30 mmol) was allowed to occur at −78°C (8 − 10 hr) in the presence of liquid Si_2H_6 and GeH_4. Reaction materials were removed, separated, and analyzed completely. No products containing Si-Si-Si or Si-Ge bonds were detected.

A sample of SiH_3PD_2 (0.23 mmol)[5] with BF_3 (0.78 mmol) was allowed to undergo redistribution at −78°C. After 9 hr, volatile reaction materials were separated and subjected to IR, ^1H and mass spectral analyses. Spectra of unreacted SiH_3PD_2 were superimposable with those of the initial reactant material. Pure PD_3 was obtained. The $(SiH_3)_3P$, within the limits of our experimental methods, showed complete absence of Si–D bonds.

SiH_3PH_2 and BF_3 (2:2.5 mole ratio) were combined at −196°C in a heavy-walled NMR tube and allowed to warm to −78°C. ^{31}P and ^1H NMR spectra were obtained at −80°C periodically over a 10 hr period. However, because resonance lines were broad and ill-defined, unambiguous interpretation of the spectra was not possible.

(B) *$Si_2H_5PH_2/BF_3$ or $Si_2H_5PH_2/SiH_3PH_2/BF_3$.* Reactions (Table I) were carried out and products separated as described in A, above. The lowest volatility function from the $SiH_3PH_2/Si_2H_5PH_2$ reaction, presumed from mass spectral analysis to be a $(Si_2H_5)_3P/(SiH_3)_2PSi_2H_5$ mixture could not be separated. The ^{31}P NMR spectra of $SiH_3P(Si_2H_5)_2$ and $(Si_2H_5)_3P$, not previously reported[5,8,29], are singlets at δ −351 pm and −360 ppm, respectively.

(C) *SiH_3PH_2/BCl_3 or $Si_2H_5PH_2/BCl_3$.* Reactions occur rapidly from −112°C to −78°C to form $SiH_3PH_2{\cdot}BCl_3$. The complex is stable for days at −78°C. the complex sublimes quantitatively at −23°C. It decomposes slowly at 0°C. Reaction of $SiH_3PH_2{\cdot}BCl_3$ with excess SiH_3PH_2 at −45°C, yielded unreacted SiH_3PH_2 along with SiH_3Cl, $(SiH_3)_2PH$, and $(SiH_3)_3P$ as products.

(D) *SiH_3PH_2/BBr_3.* SiH_3PH_2 (0.63 mmol) and BBr_3 (0.19 mmol) were allowed to react at −78°C. After 1 hr, PH_3 (0.02) and a SiH_3PH_2/SiH_3Br mixture (0.61 mmol) were removed at −78°C. At higher temperatures, SiH_3Br formation occurred rapidly.

(E) *SiH_3PH_2/B_2H_6 or $Si_2H_5PH_2/B_2H_6$.* Reaction of $Si_2H_5PH_2$ (0.05 mmol) or SiH_3PH_2 (0.05 mmol) with B_2H_6 (0.10 mmol) at −78°C resulted in formation of $Si_2H_5PH_2{\cdot}BH_3$ or $SiH_3PH_2{\cdot}BH_3$. The adducts alone at temperatures up to −45°C, or in the presence of excess $Si_2H_5PH_2$ or SiH_3PH_2, respectively, underwent only traces of redistribution to trisilylphosphine products.

(F) *SiH_3PH_2/B_5H_9 or $Si_2H_5PH_2/B_5H_9$.* SiH_3PH_2 or $Si_2H_5PH_2$ (0.20 mmol) were combined with B_5H_9 (0.15 mmol) at −78°C. After 24 hr at −78°C and 24 hr at 0°C, no reaction had occurred.

(G) *GeH_3PH_2/BF_3.* GeH_3PH_2 and excess BF_3 were condensed together and warmed to −112°C (Table I). White solid, presumed to be $GeH_3PH_2{\cdot}BF_3$, formed immediately. After 4.6 hr, volatile products were removed first at −112°C, and then at 25°C. The $(GeH_3)_3P$ fraction contained some BF_3, since formation of traces of GeH_3F and involatile solid accompanied its warming to 25°C.

(H) *GeH_3PH_2/B_2H_6.* GeH_3PH_2 and B_2H_6 (Table I) were allowed to react at −112°C to form $GeH_3PH_2{\cdot}BH_3$. The reaction mixture was warmed further to −45°C. Volatile reaction materials, removed at −45°C, consisted of PH_3 and B_2H_6 (as a mixture). The lowest volatility fraction, $(GeH_3)_3P$, and traces of GeH_4 were removed at 0°C.

(I) *GeH_3PH_2/B_5H_9.* GeH_3PH_2 and B_5H_9 were allowed to react at −45°C (Table I). After removal of PH_3 and B_5H_9 at −45°C, $(GeH_3)_3P$ remained.

In a separate experiment, B_5H_9 (4.03 mmol) and GeH_3PH_2 (1.00 mmol) in separate bulbs were allowed to mix in the gas phase at 25°C. A clear, low volatility liquid [$(GeH_3)_3P$] formed within 5 min.

After 40 min. the reaction contents were separated and found to consist of PH_3 (0.30 mmol), GeH_4 (0.37 mmol), B_5H_9 (4.03 mmol), GeH_3PH_2 (0.28 mmol), and $(GeH_3)_3P$ (0.20 mmol).

RESULTS AND DISCUSSION

The silylphosphines, SiH_3PH_2 and $Si_2H_5PH_2$, and GeH_3PH_2 react with BF_3, BCl_3, BBr_3, B_2H_6, or B_5H_9 to form initially Lewis acid-base complexes and subsequently, in some cases, trisubstituted redistribution products of type R_3P ($R = SiH_3$, Si_2H_5, GeH_3). SiH_3PH_2 or $Si_2H_5PH_2$ with BF_3[5,7] BCl_3,[14] BBr_3[14] or B_2H_6[8] and GeH_3PH_2 with B_2H_6[13] react between −112°C and −78°C to form 1:1 adducts:

$$RPH_2 + BX_3 \rightarrow RPH_2 \cdot BX_3 \tag{4a}$$

$$(R = SiH_3, Si_2H_5; X = F, Cl, Br)$$

$$R'PH_2 + \tfrac{1}{2}B_2H_6 \rightarrow R'PH_2 \cdot BH_3 \tag{4b}$$

$$(R' = SiH_3, Si_2H_5, GeH_3)$$

Germylphosphine and the silylphosphines also interact with B_5H_9 at low temperatures; however, because the complexes are highly dissociated, the adduct composition(s) was not clearly established. Hence, their compositions are given as $(GeH_3PH_2)_{1-2} \cdot B_5H_9$ consistent with that known for other B_5H_9-phosphine complexes.[30] Except for the SiH_3PH_2/BBr_3 and GeH_3PH_2/BF_3 systems, where decomposition with Si–P and Ge–P bond cleavage occurs even at −78°C to form SiH_3Br or GeH_3F, respectively, (Equation 3), the reaction systems are stable at low temperatures. As noted previously,[7,8,13,14] the silyl- and germylphosphine-BH_3 and silylphosphine-BCl_3 adducts are highly associated at −78°C; e.g. only traces of BCl_3 and SiH_3PH_2 can be removed from $SiH_3PH_2 \cdot BCl_3$ under high-vacuum. In contrast, BF_3 or B_5H_9 can be removed slowly at −78°C *in vacuo* from $SiH_3PH_2 \cdot BF_3$ or $(GeH_3PH_2)_{1-2} \cdot B_5H_9$, respectively, indicating that these adducts are partially dissociated. Based on the data available for the systems studied, the qualitative order of adduct stabilities (increasing degree of association) appears to be $SiH_3PH_2 \cdot B_5H_9 \cong GeH_3PH_2 \cdot B_5H_9 < SiH_3PH_2 \cdot BF_3$ (or $Si_2H_5PH_2$) $< SiH_3PH_2 \cdot BCl_3 < SiH_3PH_2 \cdot BBr_3 < SiH_3PH_2 \cdot BH_3 \cong GeH_3PH_2 \cdot BH_3$. Within the limits of our work, SiH_3PH_2 and $Si_2H_5PH_2$ appear qualitatively comparable with respect to their basicity towards borane Lewis acids.

The silylphosphine-BF_3 adducts [$SiH_3PH_2 \cdot BF_3$ and $Si_2H_5PH_2 \cdot BF_3$] at −78°C undergo slow stepwise redistribution to form mainly trisilylphosphines as:

$$2RPH_2 \xrightarrow{BF_3} PH_3 + R_2PH \tag{5a}$$

$$R_2PH + RPH_2 \xrightarrow{BF_3} PH_3 + R_3P \tag{5b}$$

From the redistribution reactions involving SiH_3PH_2 and $Si_2H_5PH_2$, high yields of $(SiH_3)_3P$ and $(Si_2H_5)_3P$ are obtained, although small quantities of $(SiH_3)_2PH$ and $(Si_2H_5)_2PH$ are formed. Similarly, a $SiH_3PH_2/Si_2H_5PH_2$ mixture with BF_3 at −78°C yields $(SiH_3)_3P$, $(SiH_3)_2PSi_2H_5$, $SiH_3P(Si_2H_5)_2$, and $(Si_2H_5)_3P$ as products.

Significant amounts of fluorosilane cleavage products can form at higher reaction temperatures; however, if the high-volatility reaction materials (e.g. PH_3 and BF_3) are removed from the reaction vessel at low temperatures before the product trisilyl- or trigermylphosphines are removed, unwanted cleavage can be minimized. Thus the redistribution reactions are synthetically viable syntheses for unsubstituted trisilylphosphines.

The rate and yield of silylphosphine-BF_3 redistribution reactions were examined as a function of reaction temperature, time, and the silylphosphine: BF_3 reactant ratio (Table I). Above −78°C, formation of unwanted fluorosilane cleavage products (as in eqn. 1) becomes significant. Below −112°C, redistribution proceeds prohibitively slowly. At −78°C, with a $BF_3{:}SiH_3PH_2$ ratio of 0.15:1.00, conversion of SiH_3PH_2 to redistribution products is only 50% complete after 12 hours. However, at a reactant ratio of 2.6:1.0 reaction is complete in 8–10 hours. Consequently, the synthesis of $(SiH_3)_3P$ appears optimized at a reaction temperature of −78°C, a reaction time of 8–10 hours, and with $BF_3{:}SiH_3PH_2$ ratios in excess of 2:1.

The $SiH_3PH_2{\cdot}BCl_3$ and $RPH{\cdot}BH_3$ ($R = SiH_3$, Si_2H_5) adducts, even with excess silylphosphine present, undergo only very slow redistribution at −78°C. However the expected Si-P bond cleavage/decomposition reaction (eqn. 3; $X = Cl$) along with small amounts of silylphosphine redistribution occur upon warming the $SiH_3PH_2{\cdot}BCl_3$ above −23°C. The $SiH_3PH_2{\cdot}BCl_3$ adduct appears more stable than originally reported;[14] we find that it is quantitatively sublimable at −23°C.

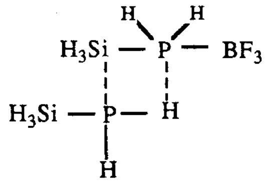
The $SiH_3PH_2{\cdot}BBr_3$ adduct could not be isolated or maintained at temperatures which allowed redistribution without extensive decomposition. Even as it formed at −78°C, large amounts of SiH_3Br formed, along with detectable quantities of $(SiH_3)_2PH$, $(SiH_3)_3P$, and PH_3. Yields of redistribution products were increased only slightly by the presence of additional SiH_3PH_2.

The borane-promoted GeH_3PH_2 redistribution processes parallel those of the silylphosphines, except that the germylphosphine-acid adducts are more susceptible to acid cleavage of the Ge–P bonds and the redistributions appear more facile. The $GeH_3PH_2{\cdot}BF_3$ complex at −78°C undergoes slow redistribution, accompanied by significant cleavage, to produce $(GeH_3)_3P$ and GeH_3F. With B_2H_6, GeH_3PH_2 again undergoes redistribution with some formation of GeH_4 as cleavage product. Most significant is the reaction with B_5H_9. GeH_3PH_2 with B_5H_9 at −45°C yield $(GeH_3)_3P$ quantitatively with little evidence of competing cleavage. B_5H_9 is recovered quantitatively upon completion of the reaction. In comparison, SiH_3PH_2 with B_5H_9 showed no detectable redistribution to $(SiH_3)_3P$. Of the systems we studied, the GeH_3PH_2—B_5H_9 system appears best for the synthesis of $(GeH_3)_3P$.

Our studies of silyl- and germylphosphine-BF_3, BCl_3, BBr_3, BH_3, and B_5H_9 complexation and adduct redistribution allow tentative conclusions to be made about the reactions. First, redistribution occurs best for complexes of intermediate degrees of association or in systems where both complexed and uncomplexed silyl- and/or germylphosphine are present. This is supported by the observation that redistribution of $SiH_3PH_2{\cdot}BCl_3$, a complex which appears highly associated at −78°C, is not observed unless excess SiH_3PH_2 is present. Secondly, redistribution reactions 5a and 5b appear to involve SiH_3 group and not SiH_2 unit transfer.

Two experiments support this conclusion. SiH_3PH_2, when allowed to undergo BF_3-promoted redistribution in the presence of liquid GeH_4 or Si_2H_6, yielded no product containing Si–Si–Si or Si–Ge bonds. GeH_4 and Si_2H_6 are known to be effective trapping molecules for singlet SiH_2 in other systems.[31] Also, the SiH_3PD_2—BF_3 redistribution produced only $(SiH_3)_3P$,[5] showing that no deuterium atoms had been transferred to Si atoms during reaction.

A possible mechanism for silyl- or germylphosphine redistributions, which is consistent with our experimental observations, might involve a four-center intermediate (SiH_3 and BF_3 used for illustration) as:[5]



In this system the role of the BF_3 might be to lower the activation energy of the redistribution process. Coordination of BF_3 to one SiH_3PH_2 molecule could inductively increase the electrophilicity of the SiH_3 group, making it more susceptible to phosphine coordination and inclined to associate with a free SiH_3PH_2 to form the new Si–P bond of the Si_2P unit. Alternatively, in the four-center complex (as shown above, but without the coordinated BF_3) the upper right phosphorus atom would form about two and one-half bonds to the hydrogen atoms and about one half bond to the silyl group. Since phosphines become less basic upon replacement of H atoms by SiH_3 groups,[6,8,14] one might expect the four-center complex to be a stronger Lewis base than a free silylphosphine molecule. Boron trifluoride coordination might stabilize the four-center complex more than it stabilizes the free silylphosphine, thus lowering the activation energy for the redistribution reactions.

Our studies show that Lewis acid promoted redistribution reactions can be effective syntheses for unsubstituted trisilyl- and trigermylphosphines. The possibility that Lewis acid promotion of primary organosilyl- and organogermylphosphines can be used more generally to form triorganosilyl- and triorganogermylphosphines, e.g. $(Me_3Si)_3P$ and $(Me_3Ge)_3P$, is under investigation.

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