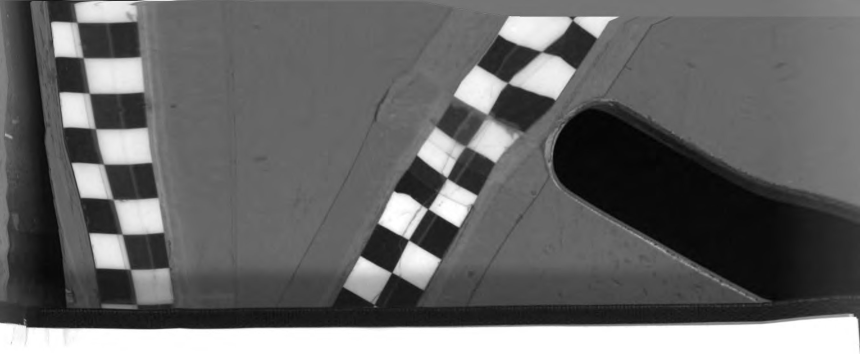


ABSTRACT

INVESTIGATIONS OF THE EQUILIBRIUM REACTIONS OF SILYLPHOSPHINES WITH AMINES AND THE REACTION OF TRIMETHYLSILYLDIPHENYLPHOSPHINE WITH NICKEL HALIDES

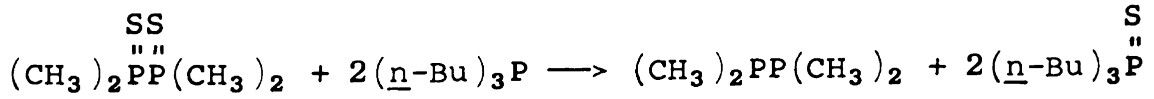
By

Ronald Eugene Goldsberry

The purpose of this study was to synthesize phenyl and methyl substituted trimethylsilylphosphines and to investigate their equilibrium reations with amines. The possibility of obtaining stable silylphosphine adducts with nickel halides was also investigated.

Two silylphosphines, trimethylsilyldiphenylphosphine (I) and trimethylsilyldimethylphosphine (II) were prepared according to the following equations where R = CH_3 or Ph:

$$2Ph_2PCl + 2Na \longrightarrow Ph_2PPPh_2 + 2NaCl$$



$$(CH_3)_2\overset{S}{\overset{\|}{P}}\overset{S}{\overset{\|}{P}}(CH_3)_2 + 2(\underline{n}\text{-Bu})_3P \longrightarrow (CH_3)_2PP(CH_3)_2 + 2(\underline{n}\text{-Bu})_3\overset{S}{\overset{\|}{P}}$$

$$R_2PPR_2 + 2M(\text{Na or Li}) \longrightarrow 2R_2PM$$

$$R_2PM + (CH_3)_3SiCl \longrightarrow R_2PSi(CH_3)_2 + MCl.$$

The equilibrium constants for the reactions of (I) and (II) with amines as indicated by the following equation were obtained as a function of the type of amine used in the reaction,

$$Me_3SiPR_2 + HNR'_2 \rightleftharpoons Me_3SiNR'_2 + HPR_2.$$

For both (I) and (II), the primary aromatic amines were observed to exchange to a slightly greater extent than the primary aliphatic amines which exchanged to a greater extent than the secondary aliphatic amines. The values of the equilibrium constants also indicated that for a particular amine, (I) exchanged to a greater extent than (II).

The following explanations were offered to help rationalized the results of the equilibrium studies. First, as is expected, the silylamines formed from secondary aliphatic amines are less stable than those from primary aliphatic amines. Similarly, silylphosphines with bulky phenyl groups are less stable than silylphosphines with methyl groups. Second, the primary aromatic aminosilanes are more stable than their aliphatic analogs possibly because of the extra stabilization present in the aromatic aminosilanes from conjugation of the silicon-nitrogen π-bond ($d\pi$-$p\pi$) with the aromatic ring. In contrast to this type of stabilization in aromatic aminosilanes, such effects in the aromatic phosphinosilane (I) appear to be not as effective. Third, the silylamines as a class of compounds are more stable than the silylphosphines. This may be rationalized by suggesting that the silicon-nitrogen bond is more stable than the silicon-phosphorus bond.

The adducts $NiX_2(PPh_2SiMe_3)_2$ were formed from the reactions of (I) with nickel halies (Br, I). The structures of these adducts have been designated as diamagnetic square-planar. Also obtained as products of these reactions were the adducts $Ni(PPh_2)_2[PPh_2Si(CH_3)_3]_2$ (III) and $NiX_2(HPPh_2)_{2\text{ or }3}$ (IV). The adduct (III) resulted from the cleavage of the Si-P bond in (I) and (IV) resulted from the hydrolysis of (I).

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By

Ronald Eugene Goldsberry

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DEDICATION

To My Wife, Betty

and

Our Parents

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INTRODUCTION

Nomenclature

The Committee on Nomenclature of the American Chemical Society and the Commission on the Nomenclature of Organic Chemistry of the International Union of Pure and Applied Chemistry have adopted a system for naming organosilicon compounds.[1,2] Compounds derived from the structure H_3SiNH_2 are called silylamines, with the use of the appropriate prefixes to designate substitution. Similarly, compounds derived from the structure H_3SiPH_2 are called silylphosphines. This system of prefix designation for nitrogen or phosphorus substitution becomes quite cumbersome when more than one nitrogen or phosphorus is attached to silicon. In these cases, the amine or phosphine grouping is designated as a substituent of the silane.

The generic name silazane is given to the series $H_3Si(NHSiH_2)_nNHSiH_3$ and likewise the name silphosphane is given to the series $H_3Si(PHSiH_2)_nPHSiH_3$. Compounds of this series are called disilphosphanes, trisilphosphanes, etc. depending upon the number of silicon atoms in the molecule. Compounds of the type $(H_2SiNH)_n$ and $(H_2SiPH)_n$ are given the generic name cyclosilazanes and cyclosilphosphanes respectively, the prefix depends upon the number of silicon atoms in the ring.

HISTORICAL

The chemistry of silicon-nitrogen compounds has been investigated quite thoroughly. It is evident that silicon-nitrogen compounds differ markedly from their carbon analogs with respect to their chemical behavior. There have been numerous publications which dealt with this topic, and there are two excellent articles which review current activity in the field of silicon-nitrogen compounds.[3,4]

However, the chemistry of silicon-phosphorus compounds is not as well investigated, presumably because of the difficulty in preparing these compounds. Recently, however, the interest in the chemistry of these compounds has increased, with a concurrent development of better methods for their synthesis.

The interests in these compounds are varied, but the majority of the research compared their chemistry to the chemistry of the analogous nitrogen compounds. The chemistry of nitrogen and phosphorus may be expected to be similar because of similarity in the outer electronic structures of the gaseous atoms. Nitrogen does have some properties in common with the heavier elements of the group; however, it shows highly individual behavior in many important respects. For example, elemental nitrogen

consists of gaseous N_2 molecules, whereas the heavier elements form tetraatomic molecules (*e.g.*, P, P_4) and are solids at room temperature.[5]

There are several cases where sufficient differences exist between nitrogen and the succeeding members of the group to detract from the usefulness of regarding nitrogen as the prototype for the group. For example, stoichiometrically analogous halides, oxides and oxo acids of nitrogen and phosphorus are almost completely unrelated to each other whereas, those of phosphorus, arsenic and antimony are similar to each other. Therefore, it is of interest to determine the similarities and differences of the silicon-nitrogen compounds compared to the silicon compounds of phosphorus, arsenic and antimony.

Formation of a $d\pi$-$p\pi$ bond has been postulated as a characteristic of the Si-N bond.[6] Trisilylamine and tri-(methylsilyl) amine have been shown by infrared and Raman spectra[7,8,9] and electron-diffraction data[10] to be co-planar molecules.[11] Compared with the calculated (p-p) single bond in Si-N calculated from the sum of the covalent radii (variously assessed as 1.87 or 1.80 Å) and a ($p\pi$-$p\pi$) double bond in =Si=N- (1.62 Å), an interatomic distance of 1.73 ± 0.01 Å has been found for a series of Si-N compounds.[12,13] These factors have been interpreted in terms of the ability of the lone pair of electrons of nitrogen to be donated to the empty *d* orbital of the silicon ($d\pi$=$p\pi$ overlap).

The polarity of the Si-N bond in substituted trisilylamines is decreased and the basicity is lowered as compared with their methyl substituted isostructural counterparts.[14] This may be observed for example in the formation of complexes of silylmethylamines with trimethylboron;[15] neither trisilylamine nor methylsidilylamine forms a complex. Dimethylsilylamine forms a weak complex and trimethylamine forms a more stable one.

The character of the silicon-phosphorus bond is presently being debated. Davidson, et al.[16] have suggested that the heavy atom skeletons of the molecules $(SiH_3)_3P$ and $(SiH_3)_3As$ may be planar or nearly so due to the similarities of their vibrational spectra to those of trisilylamine $(H_3Si)_3N$. An extended Hückel molecular orbital treatment by Cowley[17] has led to a claim that the most stable configuration for trisilylphosphine should be planar. These results may be rationalized by postulating that the silicon-phosphorus bond does have some $d\pi$-$p\pi$ character. However, some authors have taken an agnostic view of the supposedly large (p-d)-π contributions to silicon not only for the silicon-phosphorus bond, but for the Si-Ge and Si-N bonds as well.

Randall and Zuckerman[18] calculated spin-spin coupling constants for several compounds and related these values to the amount of s-character in a bond. For silicon-nitrogen compounds, the amount of s-character in a nitrogen hybrid increases with $d\pi$-$p\pi$ bonding. This is based on the

assumption that the $d\pi$-$p\pi$ bond is formed from an orbital on nitrogen having perhaps pure p character.[19] These nmr results obtained by Randall and Zuckermann led them to take a skeptical view on the proposed ability of phosphorus and nitrogen to donate their lone pair of electrons to the empty d-orbitals of silicon. However, Ebsworth[20] has since pointed out that there may be considerable overlap between a π-type d-orbital of silicon and a nitrogen lone pair which is SP^3 in character, so that the amount of s-character in a nitrogen hybrid does not necessarily have to increase with $d\pi$-$p\pi$ bonding. Zuckermann's skepticism of the $d\pi$-$p\pi$ bond is also supported by force constant data which depicts single-bond character for the Si-N and Si-P bonds[21,22] rather than double bond character. Finally Beagley, et al.[23] has shown by electron diffraction data that the heavy atoms of trisilylphosphine, $(SiH_3)_3P$ and trisilylarsine $(SiH_3)_3As$ are not coplanar as might be expected if appreciable $d\pi$-$p\pi$ character existed. The bond length was determined to be 2.25 Å while the predicted single bond length calculated by adding the required Pauling covalent radii is 2.27 Å. These experiments may suggest that the ability of phosphorus to donate its p electrons to atoms which contain empty d-orbitals (that is, silicon) is not experimentally verifiable.

Synthesis of Silicon-Nitrogen and Silicon-Phosphorus Compounds

The most common method of establishing a bond between silicon and nitrogen is by the action of ammonia or primary and secondary amines on halosilanes. Data which relate the comparative yields of silylamines produced when sterically hindered halosilanes and amines are allowed to interact with each other as a function of the halogen on the halosilane is not available; therefore, the differences in the reactivity of the halogens on the halosilane have not been established with any degree of certainty. From the data available, the bromo- and iodo-silanes appear to be more reactive toward a given amine than do the chlorosilanes.[24] Because of their availability, however, the chlorosilanes are most frequently employed in synthesis. The halide ion produced during the reaction is precipitated as the amine hydrohalide. The reaction is reversible and the halosilane can be obtained from the silylamine and the amine salt.[25]

$$R_3SiCl + 2R'NH_2 \rightleftharpoons R_3SiNHR' + R'NH_3Cl$$

The product of the reaction of a monohalosilane with ammonia or an amine depends upon the electronic and steric nature of the reactants and products. A silylamine, disilazane or a trisilylamine may be formed. When the non-halogen substituents attached to silicon are hydrogen, there is a definite tendency for complete silylation of the amine.[26,27,28] For example, when silylchloride is treated with ammonia,

trisilylamine can be obtained in 80 percent yield.[26] The product of the reaction is dependent on the size of the alkyl substituent on silicon. The tendency for complete silylation of the amine is decreased as the size of the groups attached to silicon is increased. When trimethylchlorosilane is allowed to react with ammonia, only hexamethyldisilazane can be isolated.[29,30,31,32,33] In contrast to the results obtained with trimethylchlorosilane, the preference for formation of silylamine is observed in the reaction of triethylchlorosilane with ammonia. In this reaction, triethylsilylamine is the major product, the disilazane is the minor product.[34,35] With higher trialkylchlorosilanes, only silylamines have been reported as products.[36,37] The reaction of a dihalosilane with ammonia or an amine results in the formation of a silylamine, a silazane, or a polysilazane (see Table I) depending upon the nature of the reactants and the reaction conditions. With dihalosilanes in which there is little hindrance, the cyclosilazanes and the polysilazanes predominate, while with sterically hindered dihalosilanes, compounds with the diamine, $(R_2N)_2SiR'_2$, structure can be isolated. The reaction of trihalosilanes and tetrahalosilanes with ammonia results in the formation of polysilazanes. (See Table I).

In contrast to the method of preparation of silicon-nitrogen compounds, there has been no reported method of formation of a silicon-phosphorus bond by the action of phosphine on a chlorosilane. The first reported preparation

Table I. Synthesis of silicon-nitrogen compounds from dihalosilanes and higher halosilanes.

Halosilane	Amine	Product	Reference
H_2SiCl_2	NH_3	Polysilazane	38
CH_3SiHCl_2	NH_3	Polysilazane	39
$(CH_3)_2SiCl_2$	NH_3	Polysilazane	40
		$[(CH_3)_2SiNH]_3$	39
		$[(CH_3)_2SiNH]_4$	39
$(CH_3)(C_2H_5)SiCl_2$	NH_3	$[(CH_3)(C_2H_5)SiNH]_3$	41
(tert-C_4H_9)$(CH_3)SiCl_2$	NH_3	(tert-$C_4H_9(CH_3)Si(NH_2)_2$	42
$(C_6H_5)_2SiCl_2$	NH_3	$[(C_6H_5)_2SiNH]_3$	43
$HSiCl_3$	NH_3	Polysilazane	44
$HSICl_3$	$(C_2H_5)_2NH$	$HSi[N(C_2H_5)_2]_2Cl$	45
$SiCl_4$	NH_3	Polysilazane	38
$SiCl_4$	$(CH_3)_2NH$	$[(CH_3)_2N]_4Si$	46

of a silylphosphine in the literature involved heating silane, SiH_4, and phosphine, PH_3, in a tube at 450^0 to give H_3SiPH_2.[47,48] Disilanylphosphine, $Si_2H_5PH_2$, and disilphosphane, $(SiH_3)_2PH$, were prepared directly from phosphine and silane or disilane by silent-electric-discharge methods.[49,50] Silylphosphines have also been prepared directly from elemental phosphorus as described by the following equation:[51]

$$H_3SiI + \underset{(white)}{P} \xrightarrow[0^0]{\text{sealed tube}} P(SiH_3)_3 + (H_3Si)_2PI + H_3SiPI_2 + (SiH_3)_4PI$$

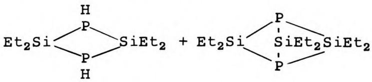
The most convenient and general method of obtaining silicon-phosphorus compounds involves the reaction of alkali metal (lithium, sodium and potassium) phosphides with halosilanes (chloro, bromo and iodo). There is not sufficient data available to determine which of the alkali metal phosphides is the most reactive to a given halosilane; however, the reactions of lithium phosphides with chlorosilanes are the ones most frequently used. This is probably because of the relative ease of obtaining the lithium phosphides from butyl lithium. As already mentioned, the chlorosilanes are employed more frequently because of their availability.

A mixture of lithium phosphides are obtained when phosphine is treated with butyl lithium according to the following equation:[52]

$$Ph_3 + n\text{-}BuLi \xrightarrow{\text{ether}} LiPH_2 + Li_2PH + Li_3P$$

When these lithium phosphides are allowed to react with trimethylchlorosilane, the mono-, di- and tri-substituted silylphosphines are obtained.[51] Cyclosilphosphanes are obtained when diethyldichlorophosphine, Et_2SiCl_2, is added to the mixture of lithium phosphides.[51] This reaction is described by the equation:

$$\text{(Phosphide mixture)} + Et_2SiCl_2 \xrightarrow[0^0]{\text{ether}}$$



The reactions of other alkaliphosphides with halosilanes are reported in Table II along with the products obtained from these reactions.

Table II. Synthesis of silicon-phosphorus compounds from alkali metal phosphides and halosilanes.

Halosilane	Alkali Metal Phosphide	Products	Ref.
Me_3SiCl	$LiPEt_2$	Me_3SiPEt_2	53a
Me_2SiCl_2	$LiPEt_2$	$Me_3Si(Cl)PEt_2 + (Et_2P)_2SiMe_2$	53a
$SiCl_4$	$LiPEt_2$	$Si(PEt_2)_4$	53b
Me_3SiCl	$NaP\Phi_2$	$Me_3SiP\Phi_2$	54
H_3SiBr	KPH_2	$P(SiH_3)_3$	55
Me_3SiF	KPH_2	$(Me_3Si)_2PH$, $(Me_3Si)_3P$	56

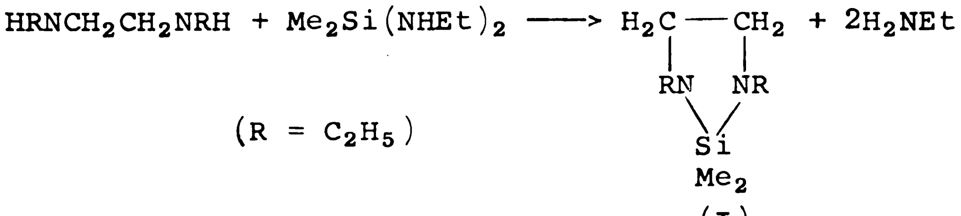
Finally, silicon-phosphorus compounds may be obtained from the reaction of silyl-lithium compounds with halo phosphines.[57] This method is limited, however, to triphenyl and other phenylated silyl-lithium compounds. (Whereas trialkylsilyl lithium compounds have at most only a transitory existence, the stability of phenylated silyl-lithium compounds has been attributed to delocalization of the negative charge over the aromatic portion of the molecule).[58,59] The reactions involving silyl-lithium compounds are further complicated from the fact that only small yields are obtained. The silyl-lithium compounds are most easily prepared in solvents like tetrahydrofuran (THF) and other cyclic ethers.[60] However, the silyl-lithium compounds react with the THF under the conditions at which the reaction is run.[61] Therefore, the yield of the silylphosphine is reduced.

Exchange Reactions of Amines with Silylamines

In 1949 Larson *et al*.[37] demonstrated that N(triethylsilyl)ethylamine underwent an exchange reaction when heated with primary amines according to the equation:

$$Et_3SiNHEt + H_2NR \longrightarrow Et_3SiNHR + H_2NEt$$

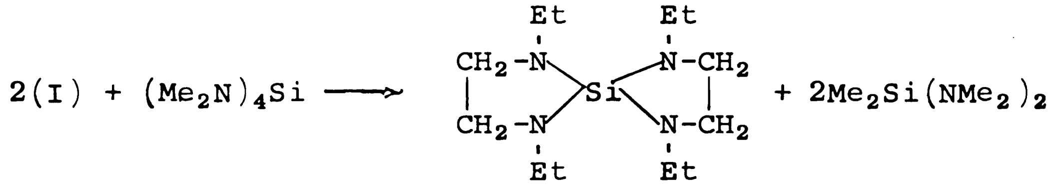
Since Larsson's work, new silylamines have been prepared from readily available silylamines by this route. Abel and Bush[62] found that symmetrically substituted ethylenediamines reacted with a *bis*-aminosilane to give cyclic compounds according to the equation:



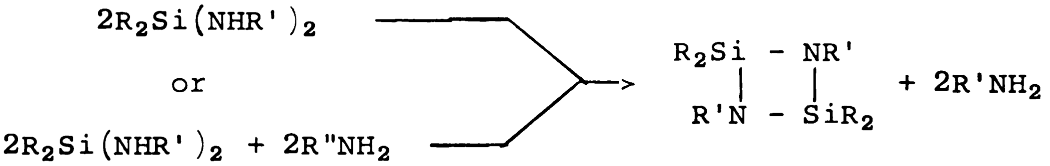
(R = C_2H_5)

(I)

The exchange of (I) with tetrakis-dimethylaminosilane led to the formation of a spirane according to the equation:



Fink[63] demonstrated that heating $R_2Si(NHR)_2$ or allowing it to exchange with a primary amine in which R or R' are bulky groups led to a cyclodisilazane.



Fessenden[64] showed that hexamethyldisilazane lost ammonia when refluxed with some secondary aliphatic and aromatic amines. In addition, the reversible nature of the reaction was demonstrated. This reaction is described by the equations:

$$Me_3SiNHSiMe_3 + 2NHBu_2 \longrightarrow 2Me_3SiNBu_2 + NH_3$$

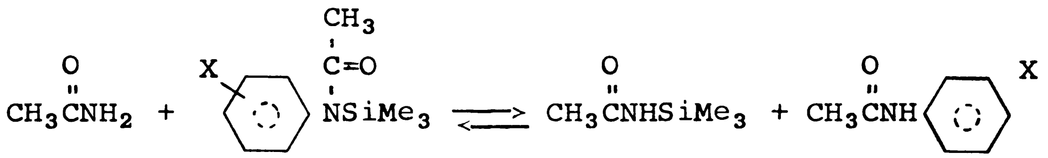
$$Me_3SiNBu_2 + \text{excess } NH_3 \xrightarrow[25^0,\ 12\ hrs]{press} Me_3SiNHSiMe_3 + HNBu_2$$

There appears to be an anomaly involved in the exchange reactions of silylamines with N-substituted anilines. It was reported that N-methylaniline did not exchange with hexamethyldisilazane and that N-ethylaniline did not exchange with hexamethylcyclotrisilazane.[65] In contrast to these reports, Tanslo[66] reported that tris-(ethylamino)propylsilane does exchange with N-methylaniline according to the following equation:

$$\underline{n}\text{-PrSi(NHEt)}_3 + \text{2PHMeNH} \longrightarrow \underline{n}\text{-PrSiNHEt(NMePh)}_2 + 2\text{H}_2\text{NEt}.$$

The differences in these results have been rationalized by considering the extent to which the substituted aniline can approach the silicon-nitrogen bond.[67]

Klebe and Bush[68] quantitatively measured the equilibria of substituted trimethylsilylacetanilides with acetamide.



When (X) was an electron withdrawing group, the equilibrium was shifted to the right; an electron donating group shifted the equilibrium to the left. The equilibrium constants were measured by means of ^{1}H nmr spectroscopy.

The equilibrium constants and rates of exchange for the reactions of aliphatic and aromatic amines with each of three dimethylaminosilanes ($\text{RMe}_2\text{SiNMe}_2$, R = Me, Ph and CH=CH_2) were also determined by means of ^{1}H nmr spectroscopy.[67] Table III gives some of the values of the equilibrium constants calculated for these reactions and Table IV gives some of the rate constants.

Table III. Equilibrium data for the exchange at 38° of amines with dimethylaminosilanes

Aminosilane	Amine	KC
Me_3SiNMe_2	Et_2NH	0.026
"	$(iso\text{-}Pr)_2NH$	0.034
"	*tert*-$BuNH_2$	0.17
"	$PhCH_2(Me)NH$	0.70
"	*m*-toluidine	7.16
"	*p*-toluidine	13.3
$PhMe_2SiNMe_2$	Et_2NH	0.05
"	(*iso*-Pr$)_2$NH	0.007
"	$PhCH_2(CH_3)NH$	0.483
"	*tert*-$BuNH_2$	0.117
"	*p*-toluidine	16.9
"	*m*-toluidine	7.3
$ViMe_2SiNMe_2$	Et_2NH	0.047
"	*tert*-$BuNH_2$	0.21
"	*m*-toluidine	8.53
"	*p*-toluidine	12.0

Table IV. Kinetic data for the exchange of amines with dimethylaminosilanes

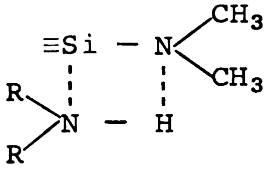
Aminosilane	Amine	Temp. ^{0}C	k (1 mole^{-1} slc^{-1})
Me_3SiNMe_2	*tert*-$BuNH_2$	38	6.4×10^{-5}
"	" (a)	38	1.9×10^{-5}
"	piperidine (a)	0	1.5×10^{-5}
"	" (a)	38	4.6×10^{-5}
"	aniline	38	5.0×10^{-4}
$ViMe_2SiNMe_2$	*tert*-$BuNH_2$	38	7.8×10^{-5}

[a] No solvent.

The study of these exchange reactions led to the following experimental results. First the primary aliphatic amines exchanged more readily on silicon than secondary amines. Second, primary aromatic amines exchanged more completely with a dimethylamino group on silicon than did aliphatic amines. Finally, electron donating groups on the aromatic ring were observed to increase the extent of the exchange. These results have been rationalized by suggesting that for the aliphatic amines the steric effect of groups on the amine nitrogen as well as the base strength of the amines are important factors which effect the magnitude of the equilibrium constants. With regard to the aromatic amines, the results were rationalized by postulating $d\pi$=$p\pi$ bonding of the aromatic nitrogen with the unfilled d orbitals of silicon. An interaction of this type would give a lower energy state

in the resulting silylamine. The effect that the groups on silicon had on the equilibrium constant or the effect of the solvent on the reaction was not completely determined.

The kinetic study indicated that the aromatic amines exchanged faster than the aliphatic amines with silyldimethylamines. The reaction was observed to be second order overall and was believed to be first order with respect to each reactant. A postulated four centered intermediate of the type shown below has been used to rationalize the kinetic data.



With respect to the silylphosphines there has been no reported attempt to study the exchange reactions of these compounds with amines or other phosphines prior to this work.

Reactions of the Silicon-Phosphorus Bond

The polarity of the silicon-phosphorus bond contributes to a high thermal stability of the bond but, at the same time, is responsible for its susceptibility to cleavage by polar compounds. Therefore, most reactions of silicon-phosphorus compounds with non-metal and transition-metal halides have resulted in the cleavage of the bond. However, there have been some examples reported in the literature in which stable adducts have been formed.

The silicon-phosphorus bond is cleaved by water to produce the corresponding phosphine. The alkaline hydrolysis of silylphosphines has been used for the quantitative determination of the phosphine group.[69]

$$(Et_2P)_4Si + 4H_2O \xrightarrow[OH^-]{\Delta} Si(OH)_4 + 4Et_2PH$$

Halogens and interhalogens caused cleavage of the silicon-phosphorus bond to produce the corresponding organophosphorus and silicon halides.[70] In the case of the interhalogens the more electronegative halogen attached to silicon as expected. A typical reaction is illustrated by the following equation:

$$Ph_2PSiMe_3 + Cl_2 \longrightarrow Ph_2PCl + Me_3SiCl$$

Diphenylboron chloride and trimethylsilyldiphenylphosphine produced diphenylborondiphenylphosphide according to the equation:[70]

$$Ph_2PSiMe_3 + Ph_2BCl \longrightarrow Ph_2PBPh_2 + Me_3Si\ Cl$$

Iododimethylarsine caused cleavage of the silicon-phosphorus bond in the silylphosphine to release iodotrimethylsilane.[70] Instead of the other expected product, diphenylphosphidodimethylarsine, tetraphenyldiphosphine and tetramethyldiarsine were obtained.

$$Me_3SiPPh_2 + Me_2AsI \longrightarrow Me_3SiI + Ph_2PAsMe_2 \longrightarrow (Me_2As)_2 + (Ph_2P)_2 \ .$$

Abel[71] has found that certain compounds cleaved the silicon-phosphorus bond by insertion. The silicon-phosphorus bond was cleaved by carbon dioxide according to the equation:

$$Me_3SiPPh_2 + CO_2 \longrightarrow Me_3SiO\overset{O}{\overset{\|}{C}}PPh_2 \quad \text{or} \quad Me_3Si\overset{O}{\overset{\|}{C}}OPPh_2$$

I II

Two structures are possible for the product (I) and (II). The authors did not differentiate between the two alternatives by physical evidence, but favored structure (I) on the basis of a C-O stretching frequency at 1682 cm^{-1} which agreed closely[72] with the corresponding nitrogen compound analogous to (I).

Carbon disulfide reacted similarly to carbon dioxide to produce the compound $Me_3SiSCSPPh_2$, the structure of which was not determined.[71]

Both ethyl and phenyl isothiocyanates reacted with trimethylsilyldiphenylphosphine according to the equation:[71]

$$Me_3SiPPh_2 + RNCS \longrightarrow Me_3SiN(R)CSPPh_2 (III) \text{ or}$$
$$Me_3SiC(S)N(R)PPh_2 (IV)$$

Two structures are possible for the products (III) and (IV) and both have been claimed for various insertions of isothiocyanates in similar systems.[73] Structure (III) was the favored on the basis of results of methanolysis which produced methoxytrimethylsilane and $NH(R)C(S)PPh_2$. The NH linkage in $HN(R)C(S)PPh_2$ was suggested by the infrared spectrum.

The product of the interaction of trimethylsilyldiphenylphosphine and ketene (see the equation below) showed a strong carbonyl stretching mode in the infrared spectrum at 1671 cm^{-1} indicating insertion of the carbon-carbon double bond rather than the carbonyl group.

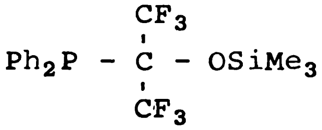
$$Me_3SiPPh_2 + CH_2{=}C{=}O \longrightarrow \underset{(V)}{Ph_2PCH_2(CO)SiMe_3} \quad \text{or} \quad Ph_2P(CO)CH_2SiMe_3 \ (VI)$$

Spectroscopic data was used to differentiate between the two possible structures (V and VI). The carbonyl stretching mode which was observed at 1671 cm^{-1} is considerably higher than that reported[79] for the monsilyl ketones (the carbonyl group in V would be essentially in a monosilyl ketone environment). Also, the chemical shift of the Me_3Si protons at 0.00 ppm and the methylene doublet ($J_{P\,H}$ = 6.5 cps) virtually rule out structure (V).

Although silylphosphines do not appear to undergo insertion into the carbonyl group of ketene, they do insert under mild conditions into the carbonyl group of hexafluoroacetone. The reaction is described by the equation:

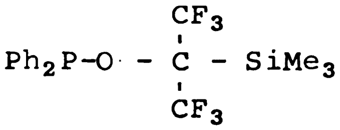
$$Me_3SiPPh_2 + (CF_3)_2CO \longrightarrow Ph_2PC(CF_3)_2OSiMe_3$$

The three possible structures for the product of this reaction are listed below.



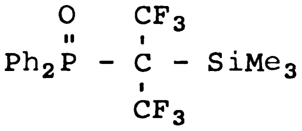
$Ph_2P-\underset{CF_3}{\overset{CF_3}{C}}-OSiMe_3$

VII



$Ph_2P{-}O-\underset{CF_3}{\overset{CF_3}{C}}-SiMe_3$

VIII



$Ph_2\overset{\overset{O}{\|}}{P}-\underset{CF_3}{\overset{CF_3}{C}}-SiMe_3$

IX

Nuclear magnetic resonance data (^1H and ^{19}F) indicated the presence of a mixture of two components. The minor product in the mixture was believed to have structure (VII). The chemical shift of the $Si(CH_3)_3$ protons was virtually identical to the chemical shift of -0.23 ppm reported[75] for the very closely analogous compound $HC(CF_3)_2OSiMe_3$. These protons showed the expected absence of coupling with fluorine and phosphorus nuclei. The nmr data indicated that the major product of the reaction was structure (IX) rather than (VIII). The ^1H nmr spectrum showed P(V)-H coupling and a coupling constant of 21 cps was observed for the coupling between fluorine and phosphorus nuclei in the ^{19}F nmr spectrum. Structure IX contains phosphorus in the +5 oxidation state and also has interatomic distances short enought to agree with the nmr data; whereas, structure (VIII) is not compatible with the nmr data. The formation of structure (IX) was rationalized by suggesting that the ester (VIII) underwent an Arbuzov rearrangement to (IX).

The fission of the silicon-phosphorus bond by transition-metal halides produced phosphido-complexes of the metals in some instances and in others the metal halide was reduced to the metal. Similar results have been reported for the reaction of disilthianes with metal halides. Abel[76] found that thiosilanes and disilthianes did not form stable co-ordination complexes with transitional and post-transitional metal halides, but invariably underwent fission of the silicon-sulfur bonds to give alkyl/arylmercaptides, sulfides or sulphonium derivatives of the metals.

Copper (I) chloride, bromide and iodide was observed to dissolve in trimethylsilyldiphenylphosphine, possibly to form some variety of phosphine-copper-halide coordination complex.[70] Subsequent heating of the copper chloride solution produced chlorotrimethylsilane and copper diphenylphosphide. The reaction is described by the following equation:

$$(Ph_2PSiMe_2)_nCuCl(?) \longrightarrow [Ph_2PCu]_n + Me_3SiCl$$

Silver chloride, bromide and iodide were all instantly reduced to silver metal with the concomitant formation of tetraphenyldiphosphine and the corresponding halogenotrimethylsilane[70] (see equation below).

$$Ph_2PSiMe_3 + AgX \longrightarrow Ag + Ph_4P_2 + Me_3SiX \quad (X = Cl, Br, I).$$

Mercury(II) chloride, bromide and iodide were reduced to mercury with the formation of tetraphenyldiphosphine and the trimethylsilyl halide.[70]

Nickel chloride cleaved the silicon-phosphorus bond in trimethylsilyldiphenylphosphine to produce nickel diphenylphosphide[70] (see equation below). The molecular weight determination of the complex in benzene indicated a degree of polymerization of about 5-6, but the low solubility and the extreme air sensitivity of the complex made precise measurements difficult.

$$NiCl_2 + Ph_2PSiMe_3 \longrightarrow [(Ph_2P)_2Ni]_n + Me_2SiCl$$

The reaction between Me_3SiPPh_2 and the pentacarbonyl halides of manganese and rhenium under mild conditions led to the known[77] dimeric species $[M(CO)_4P(C_6H_5)_2]_2$ [78]. The overall reaction is represented by the following equation:

$$2M(CO)_5Br + 2Me_3SiPPh_2 \longrightarrow [M(CO)_4PPh_2]_2 + 2Me_2SiBr + 2CO$$

$$(M = Mn \text{ and } Re)$$

A repetition of this reaction under more vigorous conditions for prolonged periods resulted in the predominant formation of the trimeric, tricarbonyl species $[M(CO)_3PPh_2]_3$. The reaction may be represented by the equation:

$$3M(CO)_5Br + 3Me_3SiPPh_2 \longrightarrow [M(CO)_3PPh_2]_3 + 3Me_3SiBr + 6CO.$$

Silylphosphines react with boron acceptors to form adducts of variable thermal stability. At high temperatures, the adducts decomposed to give halosilanes and phosphinoboron compounds.

Monosilylphosphine reacted with BF_3, BCl_3, B_2H_6 and B_2H_5Br to form adducts which decomposed to give uncharacterized glass-like polymers and monohalosilanes.[79,80,81] Table V gives the adducts which were formed, their formation and decomposition temperatures, and also the products from the decomposition reaction.

Table V. Reactions of monosilylphosphine with boron trichloride, diborane, monobromodiborane and boron-trifluoride.

$$\underset{A}{H_3SiPH_2} + \underset{B}{BX_3} \longrightarrow \underset{C}{H_3SiPH_2 \cdot BX_3} \longrightarrow \underset{D}{H_3SiX} + \underset{E}{(H_2PBX_2)_x}$$

BX_3	Adduct (C)	Formation T (^0C) of Adduct	Decomposition T (^0C) of Adduct	Decomposition Products
BF_3	$H_3SiPH_2 \cdot BF_3$	-134	-96	$(H_2PBF_2)_x$ $(H_3Si)_3P$ BF_3
BCl_3	$H_3SiPH_2 \cdot BCl_3$	- 78	-23	$(H_2PBCl_2)_x$
B_2H_6	$H_3SiPH_2 \cdot BH_3$	- 78(pres.)	-25(pres.)	$(H_2PBH_2)_x$
B_2H_5Br	$H_3SiPH_2 \cdot B_2H_5Br$	- 78	-45	$SiH_3PH_2BH_2Br$
BH_2Br	$H_3SiPH_2 \cdot BH_2Br$	- 45	-23	$(H_2PBH_2)_x$

Nöth and Schrägle[82] investigated the adducts of boron acceptors with trimethylsilyldiethylphosphine. The reaction of diborane and BF_3 with this silylphosphine in ether gave 1:1 adducts which were thermally stable up to 80°. Above 80°,

the $Me_3SiPEt_2 \cdot BH_3$ adduct decomposed to give the trimer $(Et_2PBH_2)_3$; the $Me_3SiPEt_2 \cdot BF_3$ adduct decomposed above 100^0 to give a mixture of unidentified phosphinoborane polymers. similarly, BCl_3, BBr_3, (*i*-Pr)$_2$BCl, (BuO)$_2$BCl and $(Me_2N(_2BCl$ formed adducts with Me_3SiPEt_2 which were stable at room temperature. The adducts decomposed above 120^0 to the corresponding trimethylhalosilane and dimeric diethylphosphinoborane. The reactions are described by the general equation:

$$2Me_3SiPEt_2 \cdot BX_2X' \longrightarrow 2Me_3SiX' + [Et_2PBX_2]_2$$

$$(X = Cl,\ Br,\ \underline{i}Pr,\ OBu,\ Me_2N; \quad X' = Cl,\ Br)$$

The tendency for formation of B-P addition compounds of the type $R_3SiPR'_2BX_3$ has been arranged in the following order in the series of boron compound investigated on the basis of the inductive, steric and mesomeric effects of the substituents on boron.[82]

$$BBr_3 > BCl_3 \sim BH_3 > BF_3 > (C_3H_7)_2BCl > [Me_2N]_2BCl$$

With respect to the silyl substituent on the phosphine, the silylphosphines formed adducts with boron Lewis acids under similar conditions to those needed for the formation of the unsilylated phosphine adducts. It has been suggested that the differences in their thermal stabilities results from alternative decomposition routes rather than from changes in donor strength.[79]

EXPERIMENTAL SECTION

Reagents

Trimethylchlorosilane, phenyldimethylchlorosilane (Dow Corning Corporation), trimethylsilyldiethylamine (Aldrich Chemicals), diphenylchlorophosphine and monophenyldichlorophosphine (Alfa Inorganics, Inc.) were purified by distillation. Phosphorusthiochloride (K and K Laboratories, Inc.), and tri-n-butylphosphine (Aldrich Chemical Company, Inc.) were used without further purification. Also anhydrous nickel bromide and iodide (City Chemical Corporation) and commercial methyl bromide (J. T. Baker Chemical Company) were used without further purification. All solvents and liquid amines were dried over calcium hydride and distilled. The solid amines were recrystallized from aqueous ethanol and dried in a desiccator over magnesium sulfate.

Preparation of Trimethylsilyldimethylamine

This compound was prepared according to the method of Beattie.[83] According to this procedure, excess anhydrous dimethylamine was added to trimethylchlorosilane to give the desired product.

In a typical experiment, a 500-ml three-necked round-bottomed flask fitted with a condenser, stirrer and gas inlet tube was charged with 300 ml of xylene (distilled from sodium) and a 108.6 g sample (1 mole) of trimethylchlorosilane. Anhydrous dimethylamine was bubbled into the solution at room temperature while stirring vigorously. When the mixture became too thick to stir, it was filtered to remove the solid dimethylamine hydrochloride. The solid was washed several times with xylene and the washings were combined and added to the original filtrate. Additional dimethylamine was added to the solution and the resulting mixture was again filtered. This procedure was repeated until dimethylamine hydrochloride no longer precipitated. The material was then distilled at atmospheric pressure (746 mm) through a 4 ft Vigreaux column. The two best fractions (bp 80-86°) were redistilled through a 3 ft spinning band teflon column.

Characterization of Product

The glpc suggested that the product was greater than 99% pure. It had the following properties: bp 83-84°, (746 mm); $\underline{n}^{25}\underline{\underline{D}}$ 1.3954. The infrared spectrum exhibited a very strong absorption at 1250 cm^{-1} which may be related to a symmetric C-H deformation characteristic of $Si-CH_3$.[94] (See Figure 1, Appendix I) The ^1H nmr spectrum of the liquid dissolved in benzene showed two absorptions, one of which was assigned to methyl protons on silicon at

δ = -0.33 ppm and the other assigned to methyl protons on nitrogen at δ = -2.5 ppm. The ratio of methyl protons on silicon to methyl protons on nitrogen was 3.0:2.0. (See Figure 1, Appendix II.)

Preparation of Phenyldimethylsilyldimethylamine

The phenyldimethylsilyldimethylamine was prepared in a manner similar to that described for the preparation of trimethylsilyldimethylamine in the preceeding section and also similar to the method described by Roth.[67] In a typical reaction, a one liter three-necked round-bottomed flask equipped with a condenser, stirrer and gas inlet tube was charged with 600 cc of pentane and a sample of 341.2 g (2.0 mole) of phenyldimethylchlorosilane. Dimethylamine was bubbled into the solution at room temperature while stirring vigorously. The solid dimethylamine hydrochloride was filtered when the mixture became too thick to stir, and washed several times with hexane. The washings were added to the original filtrate and the solvent was then removed from the product by means of a rotating evaporator. The remaining material was distilled at a pressure of 30 mm through a 27 x 1.5 cm column packed with glass helicies. The fractions that were collected are listed below.

Table VI. Distillation of phenyldimethylsilyldimethylamine

Fraction	Wt (g)	B.P. (^{0}C at 30 mm Hg)	$\underline{n}^{25}$ $\underline{\underline{D}}$
1	24	103	1.4950
2	85	105	1.4958
3	101	105	1.4958
4	28	105	1.4949

Characterization of Product

Glpc suggested that fractions 2 and 3 were pure. These fractions have the following properties: bp 105^{0} (30 mm); $\underline{n}^{25}$ $\underline{\underline{D}}$ 1.4958; $\underline{d}^{25}{}_{4}$ 0.904. The ^{1}H nmr spectrum showed two absorptions, one of which was assigned to methyl protons on silicon at δ = -0.26 ppm and the other to methyl protons on nitrogen at δ = -2.4 ppm. The ratio of the two different methyl groups was 1.0:1.0.

Preparation of Diphenylphosphine

Diphenylphosphine was prepared according to the method of Kuchen and Buchwald.[54] In this procedure, sodium diphenylphosphide, prepared from diphenylchlorophosphine, was hydrolyzed with ethanol to give the diphenylphosphine. Although the initially formed product was the tetraphenyldiphosphine, the phosphorus-phosphorus bond was cleaved by the action of excess sodium to give the sodium salt. A typical run is described below:

A 250-ml pressure-equalized dropping funnel and nitrogen inlet tube were inserted through one of the side arms of a carefully dried 500-ml three-necked round-bottomed flask. A stirring rod was inserted through the main mouth of the flask and the side arm was equipped with a water condenser (fitted with a drying tube) and a thermometer. The flask was flushed with a slow stream of nitrogen before and during the reaction and 5 g (0.217 mole) of sodium chunks and 200 ml of dibutyl ether were placed in the flask. While stirring gently, the contents were heated slowly to 105°. The heating mantle was then removed. When the temperature had fallen to 99°, the stirrer was stopped and the suspension was allowed to cool to 23°. The mixture was then heated again with stirring so that the solvent was refluxing (140°) and diphenylchlorophosphine (13 g, 0.059 mole) was added drop by drop. After 4 hours, the suspension was again cooled to 23° and transferred to another 500-ml three-necked flask equipped in the previously described manner. The suspension was cooled to 0° and a 35 ml sample of ethanol was added over a 15 minute period. The mixture was then refluxed at about 140° for 30 minutes. After this time, water was added until two distinct phases were present. The ethereal phase was separated in a 1-l separatory funnel and dried with anhydrous calcium chloride. The ether was removed by means of a rotating evaporator and the remaining liquid was fractionally distilled at 5 mm pressure through a 15 x 0.5 inch column packed with glass helicies. The following fractions were collected:

Table VII. Distillation of diphenylphosphine.

Fraction	B.P. (^{0}C at 5 mm Hg)	n^{25} D
1	125-130	1.6247
2	132-135	1.6273
3	135-136	1.6263

Characterization of Product

All three fractions had similar properties; however, glpc suggested the purity of fraction three to be greater than 99%. This fraction had the following properties: bp 135^0(5 mm); n^{25} D 1.6263 [lit.[54] bp 165^0 (25 mm), n^{25} D 1.6263]. The infrared spectrum showed an absorption at 2350 cm^{-1} which may be related to a P-H stretching mode. (See Figure 2, Appendix I.) The ^1H nmr spectrum of the sample dissolved in benzene showed a doublet which may be assigned to the proton on phosphorus (J_{PH} = 168 cps) at $\delta = -4.28$ ppm. The spectrum also exhibited absorptions which may be assigned to the phenyl protons; these absorbed in the same region as the solvent at about -7.2 ppm.

Preparation of Monophenylphosphine

Monophenylphosphine was prepared as described by Pass and Sschindlbower.[84] This method involved the reduction of phenyldichlorophosphine with lithium tetrahydroaluminate in

ether. The product was obtained after hydrolysis with 1:1 hydrochloric acid. An additional product, tetraphenylcyclotetraphosphine is obtained during the reduction if the addition of the dichlorophosphine to the lithium tetrahydroaluminate is too fast. This is because of the reduction of the unreacted dichlorophenylphosphine with the already formed monophenylphosphine.

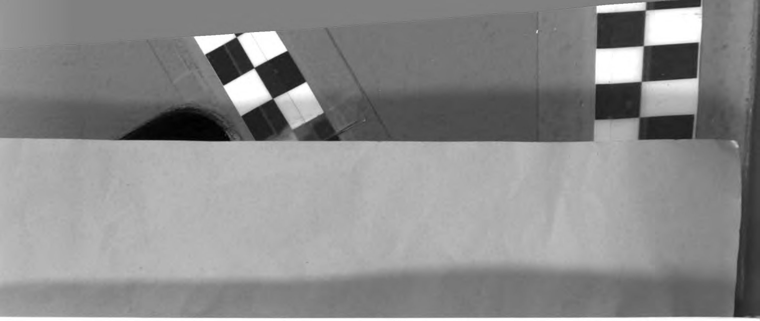
One mole (38 g) of lithium tetrahydroaluminate was added to 500 ml of ether in a dry 1-l three-necked round-bottomed flask equipped with a stirrer, 500-ml pressure-equalized dropping funnel, nitrogen inlet tube and condenser. The flask was flushed with a slow stream of nitrogen and the contents were cooled to 5°. While stirring vigorously, a 304 g (1.7 moles) sample of monophenyldichlorophosphine diluted with 200 ml of ether was added in such a manner that a temperature of +5° was not exceeded. At the end of the addition, the reaction mixture was refluxed for 30 minutes at 35°. The mixture was then cooled in an ice bath and as much 1:1 hydrochloric acid solution was added with stirring in order to give two distinct liquid phases. The two layers were separated in a 1-l separatory funnel and the upper organic layer was dried over anhydrous calcium sulfate. The ether was removed by distillation at atmospheric pressure and the remaining product was fractionally distilled at atmospheric pressure through a 15 x 0.5 inch insulated column packed with glass helicies. The following fractions were collected:

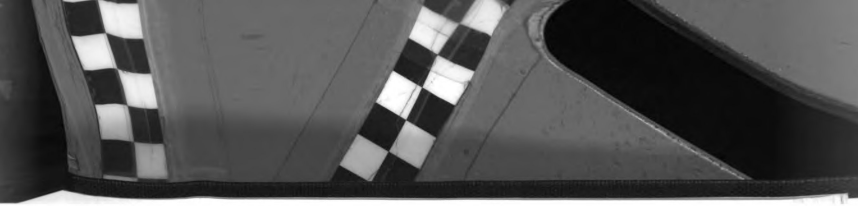
Table VIII. Distillation of monophenylphosphine

Fraction	B.P. (°C at 747 mm Hg)	n^{20} D
1	50-70	1.5011
2	70-140	1.5149
3	140-152	1.5717
4	152-155	1.5760
5	155	1.5647

Characterization of Product

On the basis of the n^{20} D, ir, ^{1}H nmr spectra and glpc, fraction 4 was shown to be the most pure fraction. Fractions 3 and 5 were also shown to be mostly monophenylphosphine contaminated with impurities. Because all of the three fractions contained water, the product was allowed to remain in contact with calcium hydride for 48 hours. The final product had the following properties: bp 158-159° (742 mm); n^{20} D 1.5794 [lit.[84] bp 160° (760 mm), n^{20} D 1.5794]. The infrared spectrum exhibited an absorption at 2350 cm^{-1} characteristic of a P-H stretching mode. The ^{1}H nmr spectrum of the product dissolved in carbon tetrachloride exhibited a doublet which may be assigned to the protons on phosphorus (J_{PH} = 200 cps) at $\delta = -3.95$ ppm.





Preparation of Tetraethyldiphosphinedisulfide

Tetraethyldiphosphinedisulfide was prepared by the reaction of ethylmagnesium bromide with thiophosphoryl chloride.[85] This compound is a very versatile intermediate for preparing compounds with two ethyl groups on phosphorus. Most other methods of preparation of such compounds give large amounts of mono- and tri-ethylated products. The grignard was prepared by reacting magnesium metal with ethyl bromide in ether.

A 36 g (1.5 moles) sample of magnesium turnings was added to 500 ml of anhydrous ether in a 1-l three-necked round-bottomed flask equipped with a mechanical stirrer, reflux condenser and dropping funnel. An 163.5 (1.5 moles) sample of ethyl bromide dissolved in 100 ml of ether was added drop by drop to the suspension of magnesium in ether with stirring. The reaction started spontaneously and the remainder of the ethyl bromide was added at a rate such that the solution boiled gently under reflux. The solution was then heated to 35^0 for one hour and cooled to 23^0. A thermometer was inserted in the flask and an 86 g (0.5 mole) sample of thiophosphoryl chloride dissolved in 100 ml of ether was added drop by drop to the grignard solution over a period of 4-5 hours. The mixture was stirred and the temperature maintained at $22\text{-}23^0$ by means of a water bath. A thick white precipitate formed during the course of the addition. The resulting slurry was heated to 35^0 for one hour to complete the reaction. The reaction products were

then carefully decomposed with as much 10% by volume sulfuric acid solution in order to give two clear phases. The top ethereal layer was separated from the aqueous layer in a 1-l separatory funnel and dried with $CaSO_4$. The ether was removed by means of a rotating evaporator. The residual oil which eventually solidified into colorless platelets upon cooling to 23° was suspended in 100 ml of methyl alcohol. The platelets were filtered and then recrystallized from a 1:1 acetone water mixture. The product was dried over phosphorus pentoxide in a vacuum desiccator. The crystal had a mp of 76-78° (literature 76-77°).[85]

Attempted
Preparation of Trimethylsilyldiethylphosphine

Trimethylsilyldiethylphosphine was prepared by a modification of the method by Fritz and Poppenburg.[52]

This method involved reaction sodium diethylphosphide with trimethylchlorosilane in dibutyl ether. The sodium diethylphosphide was prepared as described by Issleib and Tzschasch.[86]

A 500-ml pressure-equalized dropping funnel and nitrogen inlet tube were inserted through one of the side arms of a carefully dried 2-l three-necked round-bottomed flask. A stirring rod was inserted through the main mouth of the flask and the other side arm was equipped with a water cooled reflux condenser. The flask was flushed with a slow stream of nitrogen and a suspension of 67 g (2.8 moles) of sodium sand in one liter of dried dibutyl ether was heated to the

reflux temperature of the solvent (140^0) and stirred by means of a mechanical stirrer. Tetraethyldiphosphinedisulfide (60.5 g, 0.25 mole) diluted with 500 ml of dibutyl ether was added drop by drop over a 2 hour period. After heating the mixture for a total of 16 hours, it was cooled to 23^0 and the suspension of sodium diethylphosphide and sodium sulfide were transferred in an inert atmosphere to another 2-l flask. The excess sodium metal remained behind in the form of shiny lumps. In a manner analogous to that employed in the preparation of the sodium diethylphosphide, trimethylchlorosilane (108.6 g, 1 mole) dissolved in 100 ml of dibutyl ether was added drop by drop to the refluxing, stirred suspension of sodium diethylphosphide. After refluxing for an additional hour, the mixture was filtered and washed under nitrogen. The dibutyl ether was removed by distillation at atmospheric pressure. The remaining liquid was fractionally distilled at 10 mm pressure. The following fractions were obtained: (See Table IX.)

Characterization of Product

The boiling point, glpc, ^{1}H nmr spectrum and index of refraction indicated that a pure fraction was not obtained. However, a fraction was obtained that had the following properties: bp 50-53^0 (10 mm); $\underline{n}^{20}$ $\underline{\underline{D}}$ 1.4396 [lit.[52] bp 70-72^0 (20 mm)].

This fraction is believed to have the following components; Me_3SiPEt_2, Et_2PSH, and Et_2PPEt_2. The ^{1}H nmr

spectrum was too complex to interpret because of coupling of the protons from the ethyl group with phosphorus.

Table IX. Distillation of trimethylsilyldiethylphosphine.

Fraction	B.P. (^{0}C 10 mm Hg)	$n^{20}\ D$
1	43-45	1.4238
2	45-47	1.4263
3	47-50	1.4312
4	50-57	1.4396
5	67-72	1.4430
6	83-85	1.4658

Preparation of Tetramethyldiphosphinedisulfide

Tetramethyldiphosphinedisulfide, like the corresponding ethyl analog, is a valuable intermediate for the preparation of compounds containing two methyl groups on phosphorus. This compound was prepared by reacting methylmagnesium bromide with thiophosphoryl chloride.[87] The methyl grignard was prepared by the reaction of methyl bromide in ether with magnesium turnings.

A 2-l, two-necked round-bottomed flask containing 1 l of dried anhydrous ether was equipped with an inlet tube dipping below the surface of the ether and an outlet tube protected by a phosphorus pentoxide drying tube. The

flask and contents were then cooled in an ice-salt bath to 0°. Methyl bromide cooled to 20° was introduced through the inlet tube until approximately 400 g of methyl bromide was added. The flask was weighed again and the amount of methyl bromide was found to be 392.9 g. In a 3-l three-necked flask equipped with a mechanical stirrer, a reflux condenser, and a 500-ml pressure-equalized separatory funnel, a 93.9 g (3.9 moles) sample of magnesium turnings was added together with 700 ml of anhydrous ether. While stirring, the methyl bromide was added slowly to the suspension of magnesium in ether. The reaction started spontaneously and the remaining methyl bromide was added at a rate such that the ether was gently refluxing. At the end of the addition, the solution was heated to 35° for one hour. A thermometer was inserted through one of the side arms of the flask and the solution was cooled to 0-5°.

Thiophosphoryl chloride (184 g, 1.08 moles) dissolved in 100 ml of ether was added drop by drop over a period of five hours to the methyl grignard. A thick white precipitate formed during the course of the addition. After the addition, the resulting slurry was poured into a 5-l beaker containing approximately 600 g of ice. Sulfuric acid (10%) was then added with stirring over a period of 20 minutes. The product was filtered and the solid was washed with 4 l of cold water in 4 batches. It was then recrystallized from 3 l of ethyl alcohol and dried over phosphorus pentoxide in a vacuum desiccator. The final product (62.2 g, 62%)

obtained was a white crystalline solid: mp 225-227° [lit.[87] 223-227°].

Preparation of Trimethylsilyldimethylphosphine

Trimethylsilyldiethylphosphine has been prepared by the reaction of lithium diethylphosphide with trimethylchlorosilane in ether solution.[53a] The lithium diethylphosphide may be prepared by the reaction of an ether solution of phenyl lithium with diethylphosphine.[88] However, the dialkylphosphines are most conveniently prepared by the reduction of the corresponding tetraalkyldiphosphinedisulfides with lithium hydroaluminate in ether.[89] An alternative method for the preparation of trimethylsilyldimethylphosphine which eliminated the handling of the volatile dimethylphosphine involved the preparation of lithium dimethylphosphide from tetramethyldiphosphine. The latter was prepared by the reduction of tetramethyldiphosphinedisulfide with tributylphosphine.[90] The reaction of trimethylchlorosilane with lithium dimethylphosphide was most conveniently carried out in a vacuum system without solvent at -78°.

A carefully dried 500-ml three-necked round-bottomed flask equipped with a thermometer, nitrogen inlet tube and magnetic stirrer was fitted to an insulated vigreaux column 6 inches long. A standard distilling head with a thermometer and a 200 mm Liebig condenser was connected to the column. The receiving flask was a 250-ml two-necked round-bottomed flask which was equipped with a nitrogen inlet tube and a

vacuum adapter. The end of the vacuum adapter had a drying tube. The receiving flask was surrounded by a Dewar containing a slush bath of dry ice and isopropyl alcohol. Commercial tributylphosphine (81.52 g, 0.40 mole) and tetramethyldiphosphinedisulfide (37.4 g, 0.20 mole) were placed in the distilling flask and the system was thoroughly flushed with nitrogen. It was very important to maintain a positive pressure of nitrogen in the system throughout the distillation. The mixture was stirred for five minutes and slowly heated until the temperature of the distilling flask was about 250^0. As the temperature rose, the mixture became homogeneous and the product boiling at 120^0 was collected; yield 19.7 g (81%, 0.16 mole). (See Figure 2, Appendix II for the ^{1}H nmr spectrum of this compound.) The receiving flask was flushed with nitrogen through the inlet tube on the receiving flask and stoppered. In a glove bag filled with nitrogen 2.2 g (0.32 mole) of lithium chips and 100 ml of diethyl ether were added to the tetramethyldiphosphine. The flask was removed from the glove bag and fitted with a condenser containing a drying tube while maintaining a slow flow of nitrogen throughout the system. The mixture was stirred and heated for eight hours during which time a white solid was formed. The receiving flask was then fitted with a vacuum-stopcock adapter and attached to a vacuum system. The ether was removed *in vacuo* and the flask was surrounded by a Dewar of liquid nitrogen (-196^0). Commercial trimethylchlorosilane, bp 57^0 (40 g, 0.37 mole, 47 ml) which

had been previously distilled, was then distilled in vacuo at -196^0 into the flask, and the system was then allowed to warm slowly to -160^0 (petroleum-ether slush) and then again allowed to warm slowly to -78^0 (dry-ice-isopropyl alcohol). During this time, a slow reaction took place between the lithium dimethylphosphide and the trimethylchlorosilane. Periodically the stopcock on the reaction flask was closed and the flask was removed from the vacuum system and shaken to insure complete mixing of the reactants. After three hours, the system was slowly warmed to -45^0 (chlorobenzene slush) and all volatile products were distilled in vacuo to a trap held at -196^0. The impure trimethylsilyldimethylphosphine which remained in the reaction flask with the solid LiCl was permitted to warm to room temperature and distilled in vacuo into a 100 ml flask held at -196^0. Finally, the trimethylsilyldimethylphosphine trapped in the 100 ml flask was distilled at 20 mm pressure in a nitrogen atmosphere to yield the following fractions:

Table X. Distillation of trimethylsilyldimethylphosphine.

Fraction	B.P. (^{0}C 20 mm Hg)	n^{25} D
1	26-28	1.4622
2	28-33	1.4622
3	33-33	1.4622
4	33-34	1.4622

Characterization of Product

The ^1H nmr and infrared spectra (see Figure 3, Appendix II and Figure 3, Appendix I) for fractions 1-4 were very similar, and the absorptions observed were identical to those that would be expected for the compound trimethylsilyldimethylphosphine. Elemental analysis and characterization of the product by glpc were difficult to obtain because of the reactivity of the product to moisture and oxygen. The product collected (25.0 g, 58% yield) had the following properties: bp 33-34° (20 mm); n^{25}_{D} 1.4622. The ^1H nmr spectrum showed a doublet (J PH = 4.5 cps) at $\delta = -0.13$ ppm which was assigned to the methyl protons on silicon and a doublet (J PH = 2.5 cps) which was assigned to methyl protons on phosphorus at $\delta = -1.0$ ppm. The infrared spectrum showed a strong absorption at 1250 cm^{-1} characteristic of $Si-CH_3$ and a weak absorption at 420 cm^{-1} which was assigned to the Si-P stretch.[91]

The Cleavage of Tetrahydrofuran by Lithium Dimethylphosphide

Issleib and Tzschasch have reported that lithium diethylphosphide, $Li^+[(C_2H_5)_2P]^-$ decomposes when allowed to remain in contact for long periods of time with tetrahydrofuran to give a yellow, uncharacterized product.[92] In contrast to these results, Hewertson and Watson[93] suggested that lithium diethylphosphide does not undergo a chemical reaction with tetrahydrofuran, but that the solvent causes

ionization of the Li-P bond. We have found that lithium dimethylphosphide, in apparent contrast to the results reported for lithium diethylphosphide, undergoes a fairly rapid, nearly quantitative reaction with tetrahydrofuran to give $(CH_3)_2P\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}O^- \; Li^+$. This compound was not characterized, but further allowed to interact with trimethylsilylchloride, $(CH_3)_3SiCl$, which gave $(CH_3)_2P(CH_2)_4OSiMe_3$ in greater than 90% yield.

In a manner almost identical to the procedure described for the preparation of lithium diethylphosphide, a mixture of 10.9 g (0.089 mole) of tetramethyldiphosphine and 1.84 g (0.267 mole) of lithium metal were refluxed in 100 ml of tetrahydrofuran. The color of the mixture became bright yellow. After heating for six hours, excess lithium was removed by filtration. A 28.9 g (0.267 mole) sample of trimethylchlorosilane dissolved in 50 ml of tetrahydrofuran was then added drop by drop to the filtered mixture. This resulting mixture was then heated until refluxing for an additional 30 minutes to insure completion of the reaction. It was filtered and the solvent was removed by distillation at atmospheric pressure. The remaining liquid was fractionally distilled at 20 mm pressure. The following fractions were obtained:

Table XI. Distillation of product from the cleavage of tetrahydrofuran by lithium dimethylphosphide.

Fraction	B.P. °C (20 mm)
1	47-50
2	50-53
3	59-60
4	86-89
5	89-105
6	106-108

Characterization of Product

Fraction six was shown by glpc to be greater than 99% pure. The total weight of this fraction was 33 g (91% yield). The infrared spectrum displayed the expected absorptions for the molecule $(CH_3)_3SiO(CH_2)_4P(CH_3)_2$. (See Figure 4, Appendix I.) A strong peak at 1250 cm^{-1} was assigned to a symmetric C-H deformation characteristic of $Si\text{-}CH_3$. Another very strong peak at 1100 cm^{-1} was assigned to C-O stretch characteristic of SiOC.[94] Other absorptions were recorded at (cm^{-1}, intensity): 2950, 2850(vs); 2800, 2725, 1475, 1450(w); 1425(m); 1375(w); 1285(m); 1050(s); 1000(w); 965(m); 935, 900(s); 875, 850(va); 750(s); 710(m).

The ^1H nmr spectrum showed a peak at δ = -0.08 ppm which was assigned to the methyl protons on silicon, a

doublet (J PH 2.5 cps) which was assigned to methyl protons on phosphorus at δ = -0.87 ppm, broad peaks at δ = -1.42 ppm which were assigned to the methylene protons attached to phosphorus and broad peaks at -3.58 ppm which were assigned to the methylene protons attached to oxygen. (See Figure 4, Appendix II.) Integration gave a ratio of the methyl protons on silicon to the methyl protons of phosphorus of 3.0:2.0. The ^{31}P nmr spectrum showed a single absorption at δ = +53.6 ppm relative to H_3PO_4.

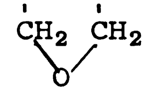
<u>Anal</u>. Calcd for $C_9H_{23}PSiO$: C, 52.40; H, 11.16; P, 15.04.
Found: C, 52.30; H, 11.08; P, 14.79.

Molecular weight: theoretical, 206; found, 226.

Although both SiOC and POC have absorptions at 1100 cm^{-1} the ^{31}P nmr and ^1H nmr showed definitely that the compound was of the type R_2PC instead of R_2POC. Compounds of the latter type, have ^{31}P chemical shifts in the region of -100 ppm relative to H_3PO_4 and ^1H chemical shifts at about -1 ppm with coupling constants of about 7 cps. Whereas compounds of the former type have ^{31}P chemical shifts in the region of +50 ppm and ^1H chemical shifts around -0.9 ppm with coupling constants around 2.8 cps.[95,96] Therefore the band at 1100 cm^{-1} can be assigned to SiOC and indicates the formula of the compound to be $(CH_3)_3SiO(CH_2)_4P(CH_3)_2$.

The reactions which were observed may be described according to the equations.

(1)



$$(CH_3)_2P\text{-}P(CH_3)_2 + 2Li + 2\ \begin{array}{c}CH_2\text{-}CH_2\\ |\qquad |\\ CH_2\quad CH_2\\ \diagdown O \diagup\end{array} \longrightarrow 2\ (CH_3)_2P(CH_2)_4O^-\,Li^+$$

(2) $(CH_3)_2P(CH_2)_4O^- Li + (CH_3)_3SiCl \longrightarrow$

$(CH_3)_2P(CH_2)_4OSi(CH_3)_3 + LiCl$.

The cleavage of dioxane by lithium diphenylphosphide has been suggested previously.[97] In a similar manner, it has been shown that alkyl and aryl phosphides can cleave ethylene oxide.[98]

Preparation of Trimethylsilyldiphenylphosphine

Trimethylsilyldiphenylphosphine has been prepared in yields above 60% by the reaction of trimethylchlorosilane with sodium diphenylphosphide in butyl ether.[54] The sodium diphenylphosphide was prepared from commercially available diphenylchlorophosphine. Although the initially formed product was the tetraphenyldiphosphine, the phosphorus-phosphorus bond was cleaved by the action of excess sodium to give the sodium salt.

a 250-ml pressure-equalized dropping funnel and nitrogen inlet tube was inserted through one of the side arms of a carefully dried 500-ml three-necked round-bottomed flask. A stirring rod was inserted through the main mouth of the flask and the other side arm was equipped with an Allihn Condenser fitted with a drying tube. The flask was flushed with a slow stream of nitrogen and a suspension of 15.22 g (0.65 mole) of sodium sand in 300 ml[99] of n-butyl ether (distilled from sodium) was heated so that the solvent was refluxing and was stirred by means of a mechanical stirrer. Diphenylchlorophosphine (33 g, 0.15 mole, 26.8 ml) diluted

with 75 ml of butyl ether was added drop by drop over a 1-hour period. After heating the mixture for a total of four hours, it was cooled to room temperature and the suspension of sodium diphenylphosphide and NaCl was transferred under a stream of nitrogen to a 1-liter three-necked round-bottomed flask. The excess sodium metal remained behind in the form of shiny lumps. Using equipment similar to that employed in the preparation of sodium diphenylphosphide, trimethylchlorosilane (49.5 g, 9.45 moles, 59 ml) dissolved in 100 ml of butyl ether was added drop by drop to the refluxing, stirred suspension of sodium diphenylphosphide over a two-hour period. After refluxing for an additional hour, the mixture was filtered and washed under nitrogen by means of a filtering stick similar to the one described by Halah.[100] The solvent was removed by distillation at atmosphereic pressure, and the residual oil was fractionally distilled at 3 mm pressure in a nitrogen atmosphere. The following fractions were collected during a typical distillation:

Table XII. Distillation of trimethylsilyldiphenylphosphine.

Fraction	B.P. °C, 3mm	n_D^{25}
1	137-141	1.6001
2	142-144	1.6008
3	144-145	1.6013
4	145-146	1.6025

Characterization of Product

Fractions 1 and 2 (24.0 g, 62%) were shown to be pure by glpc and had the following properties: bp 126-127° (1 mm); n^{25}_{D} 1.6001 [lit.[54] bp 126-127° (1 mm) n^{25}_{D} 1.6000]. The ^{1}H nmr spectrum exhibited a doublet (J PH = 4.9 cps) which was assigned to methyl protons on silicon at δ = -0.14 ppm. (See Figure 5, Appendix II.) The infrared spectrum showed a peak at 440 cm^{-1}, characteristic of the silicon-phosphorus bond.[91]

Reaction of Trimethylsilyldiphenylphosphine with Nickel Iodide in Benzene

All preparations were carried out under nitrogen. The anhydrous nickel iodide was dissolved slowly in a refluxing benzene solution of the trimethylsilyldiphenylphosphine (four moles of the ligand to one mole of the nickel iodide). The resulting solution was intensely colored. The excess nickel iodide was removed by filtration and the resulting complex was crystallized by the addition of *n*-hexane. A typical reaction procedure is described below.

A 100-ml three-necked round-bottomed flask was equipped with a reflux condenser (fitted with a drying tube containing phosphorus pentoxide), a nitrogen inlet tube and a stopper. The empty flask was weighed and a sample of 2.0 g (7.7 m moles) of trimethylsilyldiphenylphosphine was added to 50 ml of dry benzene after the flask had been flushed

with dry nitrogen. A sample of 0.59 g (1.9 m moles) of nickel iodide was added and while stirring, the mixture was heated so that the solvent was refluxing (about 86^{0}). The mixture turned green after 15 minutes and after heating the mixture for a total of three hours, it was filtered to remove excess nickel iodide. Green and brown precipitates formed when the solution was cooled and dry hexane added. The precipitate, now red, was washed several times with hexane and dried under vacuum. The filtrate, which was green, was cooled and a green precipitate formed. This precipitate was recrystallized from benzene and dried under vacuum. Finally, a third crop of crystals were obtained when the final filtrate was allowed to cool for 12 hours.

Characterization of Product

Three solids of different colors were isolated in the reaction of nickel iodide with trimethylsilyldiphenylphosphine. Table XIII gives the reaction times, solvent systems, mp, and analytical data for the different solids isolated.

The red solid isolated was diamagnetic in the solid state and its infrared spectrum showed a band at 2350 cm^{-1} which may be assigned to a P-H stretching mode. Hayter^{101} obtained $NiI_2(\phi_2PH)_2$ by the reaction of NiI_2 with ϕ_2PH in benzene. This compound was also diamagnetic in the solid state and its elemental analysis was very close to that obtained for the red solid isolated in the reaction of NiI_2

Table XIII. Experimental data for the preparation of NiI_2 complexes of Me_3SiPPh_2

Color of Solid	Reaction Time	mp	% Carbon		% Hydrogen		% Phosphorus		% Nickel		% Silicon	
			Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd
Red	3	198-200	46.08	43.4	3.25	4.59	10.48	7.47	10.19	7.08		
Dark Blue	5	158-160	50.46	43.4	3.91	4.59	10.07	7.47	7.81	7.08		
Green	12	174-176	45.69	43.4	4.08	4.59			6.71	7.08	6.18	6.78

with trimethylsilyldiphenylphosphine. The absorption spectra for the two compounds were also very similar. Therefore, it was concluded that the red solid isolated was the compound obtained by Hayter. The diphenylphosphine resulted from the hydrolysis of trimethylsilyldiphenylphosphine.

Similarly, the dark blue solid isolated was diamagnetic and its infrared spectrum exhibited a band at 2350 cm^{-1} characteristic of a P-H stretching mode. Its elemental analysis was in agreement with the analysis Hayter obtained for the five-coordinate compound $Ni(HP\Phi_2)_3I_2$, C, 49.8; H, 3.8; Ni, 7.2; P, 10.8. These results suggest, therefore, that the dark blue solid was not the four-coordinate complex $Ni(Me_3SiP\Phi_2)I_2$ or $Ni(HP\Phi_2)_2I_2$ but the five-coordinate complex previously obtained by Hayter, $NiI_2(\Phi_2PH)_3$. As with the red solid, it may be suggested that the diphenylphosphine resulted from the hydrolysis of trimethylsilyldiphenylphosphine.

The characterization of the green solid will be discussed in the next section.

Reaction of Trimethylsilyldiphenylphosphine with Nickel Iodide in the Absence of Solvent

Because the reaction of trimethylsilyldiphenylphosphine with nickel iodide in benzene presented difficulties with respect to hydrolysis, the reaction was carried out in a vacuum system without solvent. Trimethylsilyldiphenylphosphine was added to the nickel iodide in a nitrogen atmosphere

and the mixture was allowed to react in vacuo for eight hours. The volatile materials were removed by distillation in vacuo and collected at -196°. The green residue which resulted from the reaction was recrystallized from benzene.

In a typical reaction, a 100-ml three-necked round-bottomed flask equipped with standard tapered joints was fitted with a vacuum-adapter and stoppers. All the glassware was previously baked in an oven at 150° for 24 hours before use. Nickel iodide (0.59 g, 1.9 mmoles) was added in an inert atmosphere to the flask and the flask was then connected to a vacuum system and evacuated for 24 hours. The flask was then transferred to a glove bag containing a nitrogen atmosphere and 2.0 g (7.7 mmoles) of trimethylsilyldiphenylphosphine was added. The flask was again connected to the vacuum system. The mixture was stirred by means of a magnetic stirrer while the volatile products were distilled in vacuo to a trap held at -196°. The mixture changed to a green slurry after it had been stirred at room temperature for eight hours. The flask was transferred from the vacuum system to a glove bag and one of the stoppers was replaced with a nitrogen inlet tube and the adapter with a drying tube filled with phosphorus pentoxide. The flask was then removed from the glove bag and a nitrogen atmosphere was maintained in the system throughout all succeeding operations. The green slurry was dissolved in 15 ml of dry benzene and filtered to remove excess nickel iodide. Dry hexane (10 ml) was added to the filtrate and

the solution was cooled in an ice bath. Dark green crystals precipitated from the benzene-hexane solution. These crystals were collected, washed with cold hexane and dried under vacuum for 12 hours.

Characterization of Product

The green solid isolated in this experiment was the same as the one isolated in the preparation of the complex in benzene. The elemental analysis obtained for the complex was as follows:

Calcd for $NiI_2[Me_3SiP\Phi_2]_2$: C, 43.4; H, 4.59; Ni, 7.08; Si, 6.78.

Found: C, 45.69; H, 4.08; Ni, 6.71; Si, 6.18.

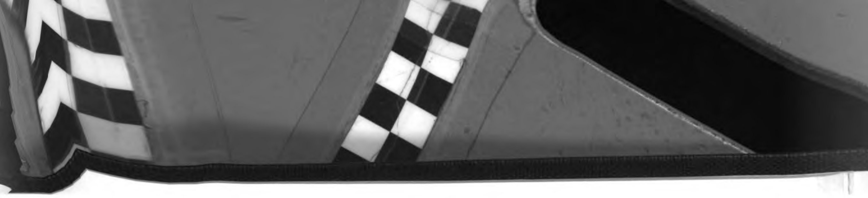
The complex dissolved readily in benzene and dichloromethane to give green solutions. These solutions decomposed on standing in solvent for long period of time. The complex was not readily oxidized, but the ligand ($Me_3SiP\Phi_2$) hydrolyzed in the presence of moisture. Magnetic measurements using $Hg[Co(NCS)_4]$ as a standard indicated that the complex was diamagnetic in the solid state. The infrared spectrum of the complex taken as a nujol mull showed a strong absorption at 1250 cm^{-1} characteristic of $Si\text{-}CH_3$. Also, the absence of a peak at 2350 cm^{-1} suggested that the diphenylphosphine complex was not present. The electronic spectra were taken in benzene solution in the region of 300-1000 mμ. The solution spectrum for the green solid was nearly

identical to the solution spectra observed for the corresponding complexes of dibutylphenylphosphine and diphenylphosphine. (Table XIV).

The spectrum consisted of: (1 a very intense absorption band at 380 mμ which was assigned to 3d-4p transitions.[102] (2) A very intense band at 460 mμ and (3) a band at 560 mμ which was probably a ligand field band.

Table XIV. Absorption spectra (λ in mμ) for NiI_2L_2 complexes

Complex	λ_{max} (mμ)	ε	Ref
$(Et_3P)_2NiI_2$	373	4690	103
	459	2900	
	610	485	
$(Bu_2PhP)_2NiI_2$	370	4040	102
	600	490	
$(BuPh_2P)_2NiI_2$	320	4350	102
	400	3460	
	500-600	sh	
	925	374	
$(HPh_2P)_2NiI_2$	380	4840	101
	460	2340	
	550	490	
$(Me_3SiPh_2P)_2NiI_2$	380	4873	
	460	2352	
	560	489	



The small amount of volatile material isolated from the reaction was characterized by ^1H nmr and infrared spectroscopy. The ^1H nmr spectrum showed an absorption at $\delta = -0.80$ ppm which may be assigned to methyl protons on silicon. The ir spectrum showed an absorption at 1250 cm^{-1} characteristic of $SiCH_3$ and a peak at 320 cm^{-1} characteristic of Si-I. This compound was not very stable. It appeared to be decomposed by light. These results indicated that the volatile material isolated from the reaction of trimethylsilyldiphenylphosphine with nickel iodide was trimethylsilyliodide.

The analytical data for the solid complex combined with the characterization of the small amount of volatile material as Me_3SiI are consistent with a nickel(II) complex of the formula $NiI_2[Me_3SiP\Phi_2]_2$. Analytical data for carbon and hydrogen may be rationalized by suggesting the presence of some $Ni(P\Phi_2)_2(Me_3SiP\Phi_2)_2$. This may be due to an elimination reaction of the type observed by Issleib[104] according to the following equation:

$$4Me_3SiP\Phi_2 + NiI_2 \longrightarrow 2Me_3SiI + Ni(Me_3SiP\Phi_2)_2(P\Phi_2)_2$$

The absorption spectrum of this complex is consistent with a square-planar structure. Particularly, no absorption was observed in the spectrum in the region of 900 mμ (ε_{max} = 300-4000) characteristic of tetrahedral complexes of the type $NiI_2(BuPh_2P)_2$.[102]

Reaction of Trimethylsilyldiphenylphosphine with Nickel Bromide in Benzene

The reaction procedure was the same as the one described previously for the reaction of nickel iodide with $Me_3SiP\Phi_2$ in benzene. The following is a typical experiment.

A 100-ml three-necked round-bottomed flask fitted with a reflux condenser, nitrogen inlet tube and a stopper was charged with a 0.51 g (2.3 mmoles) sample of nickel bromide and a 2.33 g (9.23 mmoles) sample of trimethylsilyldiphenylphosphine and then heated to the reflux temperature of the solvent (about 86^{0}). The nickel bromide dissolved slowly in the benzene and a green color appeared immediately. After heating the mixture for two hours, it was filtered in an inert atmosphere to remove excess nickel bromide. The green filtrate was cooled in an ice bath to 0^{0} and hexane was added. The green crystals which precipitated were collected on a filter and washed with hexane. The crystals were dried over phosphorus pentoxide in a vacuum desiccator. The filtrate was concentrated, cooled and hexane was added. The brown solid which precipitated was collected on a filter and dried under vacuum.

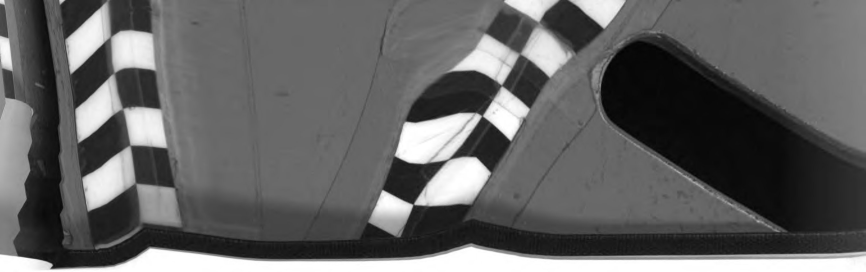
Reaction of Trimethylsilyldiphenylphosphine with Nickel Bromide in the Absence of Solvent

This reaction was analogous to the corresponding reaction with nickel iodide without solvent. In a typical experiment a 0.505 g (2.31 mmoles) sample of nickel bromide

was added to a 100-ml three-necked round-bottomed flask (previously dried in an oven) fitted with stoppers and a vacuum stopcock-adapter. The flask was connected to the vacuum system and evacuated for 24 hours. Trimethylsilyldiphenylphosphine (2.382 g, 9.24 mmoles) was then added to the flask in a glove bag filled with nitrogen. The system was evacuated again and stirred by means of a magnetic stirrer for 24 hours. The volatile material from the reaction was distilled *in vacuo* and trapped in a flask held at -196°. A green slurry remained in the reaction flask. One of the stoppers and the vacuum stopcock-adapter were replaced by a nitrogen inlet tube and a drying tube filled with phosphorus pentoxide. A nitrogen atmosphere was maintained in the system throughout the remainder of the reaction. The green solid remaining in the reaction flask was dissolved in 50 ml of benzene and filtered to remove excess nickel bromide. Hexane (15 ml) was added to the benzene solution and it was then cooled in an ice bath to 0°. The green solid which crystallized was collected on a filter and dried under vacuum.

Characterization of Product

The two solids isolated in the reaction of trimethylsilyldiphenylphosphine were soluble in benzene and methylene chloride. They appeared to be analogous to the corresponding nickel iodide complexes $(Me_3SiP\Phi_2)_2NiI_2$ and $(HP\Phi_2)_2NiI_2$.



The infrared spectrum of the brown solid taken as a nujol mull showed an absorption at 2350 cm^{-1} characteristic of P-H. A strong absorption at 1250 cm^{-1} was not observed suggesting that $Me_3SiP\Phi_2$ was not present in the complex. The ir data may be rationalized by suggesting that the ligand, $Me_3SiP\Phi_2$, was hydrolyzed to $HP\Phi_2$. Therefore, the brown solid is suggested to be the five-coordinate diphenylphosphine complex $(Ni(HP\Phi_2)_3Br_2)$ since this was the only product Hayter^{101} obtained from the reaction of diphenylphosphine with nickel bromide. The properties of the green solid were similar to those of the corresponding nickel iodide complex. The infrared spectrum showed a Si-C stretching mode at 1250 cm^{-1} characteristic of $Si\text{-}CH_3$. The spectrum did not show an absorption in the region of 2350 cm^{-1} suggesting that diphenylphosphine was not present. The solution spectrum taken in benzene in the region of 300-1000 mμ showed two bands: (1) a very intense band at 400 mμ and (2) a band at 560 mμ. This was very similar to the spectrum of the square-planar complex, $Ni(Bu_2\Phi P)_2Br_2$, prepared by Venanzi.^{102} The magnetic measurement indicated that the complex was diamagnetic in the solid state. The small amount of volatile material from the reaction was characterized by ^1H nmr and infrared spectroscopy. The ^1H nmr spectrum showed an absorption at δ = -0.62 ppm which was assigned to methyl protons on silicon. The ir spectrum showed an absorption at 1250 cm^{-1} characteristic of $SiCH_3$ and a peak at 410 cm^{-1} characteristic of Si-Br. These

results suggest that an elimination reaction had taken place to give the compound, $Ni(Me_3SiP\Phi_2)_2(P\Phi_2)_2$. Therefore, as with the nickel iodide complex, it is suggested that the complex is the square-planar $Ni(Me_3SiP\Phi_2)_2Br_2$ with a small amount of the elimination product $[Ni(P\Phi_2)_2(Me_3SiP\Phi_2)_2]$ present.

Silicon Analysis

Porcelain crucibles were fired in a muffle furnace at 700^0 to constant weight and stored in a desiccator over $Mg(ClO_4)_2$. Weighed samples (0.2-0.3 g) of the silylamine were added to the crucibles which were cooled in dry ice. Concentrated sulfuric acid (3-5 cc) was then slowly added to the samples. The crucibles were removed and allowed to warm to room temperature. They were placed in a muffle furnace and the temperature slowly raised to 900^0 over a period of 12-16 hours. The crucibles and contents were removed from the furnace and stored over $Mg(ClO_4)_2$ until cool, and reweighed to obtain the weight of SiO_2 formed. The per cent silicon was calculated using the expression

$$\% \text{ Si} = \frac{0.467 \times \text{wt } SiO_2}{\text{sample weight}} \times 100.$$

Nitrogen Analysis

The silylamines were analyzed for nitrogen by the non-aqueous titration method of Fritz.[105] Weighed samples (0.2-0.3 g) were placed in 30 to 50 cc of glacial acetic

acid and several drops of a methyl violet indicator solution added.* This solution was then titrated with a solution of $HClO_4$ in glacial acetic acid previously standardized with potassium hydrogen phthalate. The amount of nitrogen was calculated by means of the expression

$$\% \text{ N} = \frac{\text{Vol. } HClO_4 (1) \text{ x Norm. of } HClO_4 \text{ x } 14.01}{\text{Sample Weight}} \text{ x } 100.$$

Nickel Analysis

The procedure described by Coskran[106] was used to obtain the nickel analysis. A sample of 30-50 mg of the nickel compound was placed in a glass stoppered bottle and 1 ml of distilled water was added. The solution was slowly decomposed by 5 ml of concentrated HNO_3, evaporated to near dryness and then cooled slightly. A 70% solution of $HClO_4$ was added slowly and the solution was again evaporated nearly to dryness. Finally, the solution was diluted with 70 ml of water, filtered and then washed with 30 ml of water. The pH of the solution was adjusted to 6-7 with NH_4OH and an ethanol solution consisting of 1% dimethylglyoxime (DMG) was added. The volume of DMG added was determined by the relation that 1 ml approximately equals 0.0025 g of Ni. A 2 ml excess of DMG solution was added to insure complete precipitation. The solution was then

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*A solution of approximately 0.1 g of methyl violet in 10 cc of chlorobenzene.

heated so that it was almost boiling and the pH adjusted to 9-10 with NH_4OH. The solution was then allowed to stand at 23° for one hour after which time it was filtered and washed with cold water. It was also washed with 50% ethanol in case too large of an excess of DMG was added. Finally, it was dried at 110° for 1 hour. The per cent nickel was calculated using the expression.

$$\% \text{ Ni} = \frac{0.2032 \times \text{wt. of Ni(DMG)}_2}{\text{sample weight}} \times 100.$$

Infrared Spectroscopy

Infrared spectra were obtained as pure liquid films, CCl_4 solutions and nujol, hexachlorobutadiene and flurolube mulls between NaCl or KBr discs. They were also obtained on gaseous samples and KBr pellets. The instruments used included the Unicam S-P-200, Perkin-Elmer-237B and 301 spectrophotometers.

Nuclear Magnetic Resonance Spectroscopy

The ^1H nmr spectra were taken in approximately 10% solutions, with benzene as solvent and tetramethylsilane as an internal reference. The spectra were obtained on the Varian HA-100 and A-60, and Jeolco C-60 spectrophotometers. The ^{31}P nmr spectra were taken in approximately 50% solutions, with benzene as solvent and 85% H_3PO_4 as an external reference on a Varian HA-100 spectrophotometer at 40.4 Mc.

Vapor Phase Chromatography (Glpc)

The VPC analyses were obtained with an Aerograph A-90-P and F & M 810 research chromatographs with helium as the carrier gas. Each instrument was equipped with a 5 ft 20% SE-30, 60/80 chromosorb wax column.

Ultraviolet and Visible Spectrophotometry

The absorption spectra were obtained with a Cary Model 14 spectrophotometer in benzene solutions at 25^0.

Magnetic Moment Measurements

The magnetic susceptibilities of the finely divided solids were measured at room temperature on a Gouy-type balance using $Hg[Co(CNS)_4]$ as a standard.

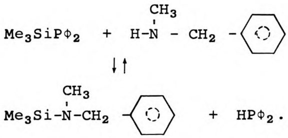
Equilibrium Reactions of Trimethylsilylphosphine with Amines

Method of Conducting Equilibrium Experiments.- All operations were conducted in a dry glove bag filled with nitrogen. All equipment and glassware were baked in an oven at 120^0 for 48 hours to eliminate water. A sample of trimethylsilylphosphine was added to a previously weighed nmr tube. Benzene was added to make the mole fraction percentage of the silylphosphine equal to 10. A sample of the amine was added and the nmr tube, which was then sealed with a nmr tube cap, was shaken thoroughly. After standing for a minimum of 24 hours at room temperature,

the proton nmr spectrum was recorded at a sweep width of 250 cps with a Varian A-60 nmr spectrometer. An HA-100 Varian nmr spectrometer was used to record the spectra with peaks having chemical shifts too small to be resolved by the Varian A-60. The spectrum was recorded six times to eliminate errors in the instrument and the peaks representing the various species were integrated with a planimeter in order to determine the relative amounts of each moiety present. The area of the peak in question was taken as an average of the six trials. This procedure was repeated twice to insure reproducible results.

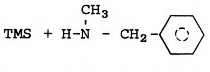
A typical example of a determination of an equilibrium constant follows:

Reaction of Trimethylsilyldiphenylphosphine with N-Methylbenzylamine

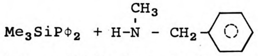


This reaction was run using relative concentrations of amine to silylphosphine of 1:1 and 2:1. In each case 1 mmole of silylphosphine was used and its concentration in the solution was adjusted to 10 mole per cent by adding the appropriate amount of benzene. The ^1H nmr spectrum of the compounds in the reaction mixture was recorded on a

Varian A-60 nmr spectrophotometer at a sweep width of 250 cps. The separation of the $H\overset{|}{N}CH_3$ from the $Si\overset{|}{N}CH_3$ peak was 5 cps and the separation of the $H\overset{|}{N}CH_2$ peak from the $Si\overset{|}{N}CH_2$ peak was 16 cps. Therefore, the amounts of the amine moieties present in the equilibrium mixture could be determined directly by relating the areas under the $H\overset{|}{N}CH_2$ and $Si\overset{|}{N}CH_2$ peak to the number of moles of each one present. The areas under the $H\overset{|}{N}CH_3$ and $Si\overset{|}{N}CH_3$ peaks were also measured and related to the amounts of the amine moieties present as a method of checking the results obtained from integration of the previously mentioned peaks. The amount of diphenylphosphine present at equilibrium was equal to the amount of the silylamine present at equilibrium. The initial number of moles of the free amine was related to the total area of the two amine peaks ($H\overset{|}{N}CH_2$ and $Si\overset{|}{N}CH_2$). The initial number of moles of the silylphosphine was related to the initial amount of free amine by the stoichiometry of the reaction. Therefore, the equilibrium number of moles of silylphosphine present was equal to the initial amount present minus the number of moles of silylamine formed. Figure 6, Appendix II shows the ^1H nmr spectra of



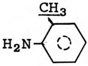
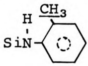
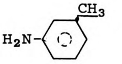
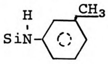
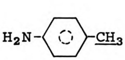
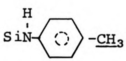
and Figure 7, Appendix II the ^1H nmr spectrum of



+ TMS. The ^1H nmr data for other equilibrium reactions are given in Table XV.

Table XV. ^1H nmr data for the exchange of trimethylsilyldiphenyl and trimethylsilyldimethyl phosphines with amines. (Recorded on the Varian A-60 spectrometer.)

$$R_2NH + Me_3SiPR'_2 = Me_3SiNR_2 + HPR'_2 \quad (R' = Ph \text{ or } Me)$$

HNR_2	$SiNR_2$	$\delta(SiNR_2)-\delta(HNR_2)$ (ppm)
$\overset{\underline{CH_3}}{HN}-CH_2Ph$	$\overset{\underline{CH_3}}{SiN}-CH_2Ph$	0.08 (Figure 7, Appendix II)
$\overset{CH_3}{HN}-\underline{CH_2}Ph$	$\overset{CH_3}{SiN}-\underline{CH_2}Ph$	0.27
$HN(\underline{CH_3})_2$	$SiN(\underline{CH_3})_2$	0.17 (Figure 8, Appendix II)
$H_2NC(\underline{CH_3})_3$	$Si\overset{H}{N}C(\underline{CH_3})_3$	0.12 (Figure 9, Appendix II)
$H_2N\overset{H}{C}(\underline{CH_3})_2$	$Si\overset{H}{N}\overset{H}{C}(\underline{CH_3})_2$	0.08
$HN(CH_2\underline{CH_3})_2$	$SiN(CH_2\underline{CH_3})_2$	0.05
$HN(\underline{CH_2}CH_3)_2$	$SiN(\underline{CH_2}CH_3)_2$	0.25 (Figure 10, Appendix II)
		0.06
		0.05
		0.03

In all cases in which the separation between the $SiNR_2$ and HNR_2 peaks was less than 0.08 ppm, the spectra were recorded on the Varian HA-100 spectrometer. The equilibrium constants for the reactions of amines with trimethylsilyldiphenyl- and trimethylsilyldimethylphosphines are listed in Tables XVI and XVII. A benzene solution of dimethylamine had to be prepared because dimethylamine boils at 7°. This solution was prepared by passing dimethylamine (Matheson, dried in a KOH, molecular sieve and CaH_2 train) through benzene cooled to 0°. The solution was titrated with 0.1721N $HClO_4$ in acetic acid.

Reaction of Trimethylsilyldiphenylphosphine with Diethylamine

A typical example of the measurement of an equilibrium constant using the Varian HA-100 spectrometer is described below. The $HN(CH_2\underline{CH_3})_2$ and $SiN(CH_2\underline{CH_3})_2$ peaks appeared as triplets; and the $HN(\underline{CH_2}CH_3)_2$ and $SiN(\underline{CH_2}CH_3)_2$ peaks appeared as quartets. The separation of the two triplets was 3 cps and the quartets 15 cps. (See Figure 10, Appendix II.) However, due to the H-H coupling constants (6.9 cps), the overlap of peaks was too great to allow an accurate measurement of the areas. Therefore, the ^1H nmr spectrum was run on the HA-100 spectrometer at a sweep width of 50 cps (see Figure 11, Appendix II). The $HN(CH_2\underline{CH_3})_2$ peaks were sufficiently separated from the $SiN(CH_2\underline{CH_3})_2$ peaks to allow their area to be calculated. Also, as with the

N-methylbenzylamine reaction, the equilibrium constant may be calculated by determining the amounts of amine moieties present by measuring the areas of the $HN(\underline{CH_2}CH_3)_2$ and $SiN(\underline{CH_2}CH_3)_2$ peaks. The equilibrium constants for this reaction are found in Table XVI.

Table XVI. Equilibrium data for the exchange of trimethylsilyldiphenylphosphine with amines

$$\underset{A}{R_2NH} + \underset{B}{Me_3SiP\Phi_2} \rightleftharpoons \underset{C}{Me_3SiNR_2} + \underset{D}{HP\Phi_2}$$

Stoichiometry A:B	R_2NH	Kc
1:1	$(\textit{iso}\text{-}Pr)_2NH$	No evidence of exchange
1:1	$PhCH_2(Me)NH$	3.99
2:1	$PhCH_2(Me)NH$	4.03
1:1	Et_2NH	4.26
2:1	Et_2NH	4.19
1:1	Me_2NH	4.89
2:1	Me_2NH	4.42
1:1	*tert*-$BuNH_2$	6.31
2:1	*tert*-$BuNH_2$	6.50
1:1	*o*-toluidine	2.86
2:1	*o*-toluidine	3.04
1:1	*m*-toluidine	6.63
2:1	*m*-toluidine	6.89
2:1	*p*-touidine	7.01
2:1	*iso*-$PrNH_2$	7.34

Table XVII. Equilibrium data for the exchange of trimethylsilyldimethylphosphine with amines

$$\underset{A}{R_2NH} + \underset{B}{Me_2SiPMe_2} \rightleftharpoons \underset{C}{Me_3SiNR_2} + \underset{D}{HPMe_2}$$

Stoichiometry A:B	R_2NH	Kc
1:1	$PhCH_2(Me)NH$	1.03
2:1	$PhCH_2(Me)NH$	1.27
1:1	Et_2NH	1.41
2:1	Et_2NH	1.33
1:1	Me_2NH	1.49
2:1	Me_2NH	1.55
1:1	*tert*-$BuNH_2$	3.45
2:1	*tert*-$BuNH_2$	3.58
1:1	*o*-toluidine	2.14
2:1	*o*-toluidine	2.02
2:1	*m*-toluidine	4.09

Reverse Equilibrium Reactions

Reactions of Diphenylphosphine with Silylamines

$$\Phi_2PH + Me_2RSiNR'_2 \rightleftharpoons Me_2RSiP\Phi_2 + HNR'_2$$

(R = phenyl or methyl; R' = methyl or ethyl)

The experimental procedure for the reverse reactions was analogous to the procedure for the forward reaction. The benzene and phosphine concentrations were adjusted so that the silicon species had the same mole percentage as in the forward reaction (10%). The position of equilibrium was measured in a manner similar to the method described earlier. The equilibrium constants calculated are listed in Table XVIII.

Table XVIII. Equilibrium data for the exchange of diphenylphosphine with substituted silylamines

$$\underset{A}{\Phi_2PH} + \underset{B}{Me_2RSiNR'_2} \rightleftharpoons \underset{C}{Me_2RSiP\Phi_2} + \underset{D}{HNR'_2}$$

Stoichiometry A:B	$Me_2RSiNR'_2$	Kc	Kc^{-1}
1:1	$Me_2\Phi SiNMe_2$	0.134	7.46
1:1	Me_3SiNMe_2	0.188	5.31
1:1	Me_3SiNEt_2	0.211	4.72

DISCUSSION OF RESULTS AND CONCLUSIONS

Four problems in the chemistry of the silylphosphines were investigated. First, the reactions of various amines with two silylphosphines, trimethylsilyldiphenylphosphine (I) and trimethylsilyldimethylphosphine (II), were investigated to determine if the amines exchanged with the silylphosphines according to equation (1).

$$(1)\quad Me_3SiPR_2 + HNR'_2 \longrightarrow Me_3SiNR'_2 + HPR_2 \quad (R = Ph \text{ or } Me)$$

Second, the reactions of phosphines with silylamines were investigated to determine if the reactions described by (1) could be run reversibly. Third, quantitative measurements of the equilibrium constants for the reactions of aliphatic and aromatic amines with silylphosphines were taken. Fourth, interactions of nickel iodide and bromide with (I) were examined to determine if stable adducts could be obtained.

The phosphines and silylamines used in these investigations were prepared by well established procedures which require no additional elaboration. However, the syntheses of silylphosphines have not been investigated as thoroughly. As a result of these studies, the following conclusions have been reached concerning the preparation of silylphosphines with phenyl or alkyl substituents on phosphorus.

The alkyl or phenyl substituted phosphinosilanes are best prepared by the action of a chlorosilane on an alkali metal phosphide rather than by the reaction of a chlorophosphine with a silyllithium compound.

Non-cyclic ethers are preferred as solvents for the preparation of the alkali metal phosphides. Cyclic ethers, for example tetrahydrofuran and dioxane, enhance the formation of the alkali metal phosphides compared to non-cyclic ethers; however, the cyclic ethers are also cleaved by the metal phosphides under the conditions at which the silylphosphines are prepared.

The silylphosphines (I) and (II) reacted with several selected aliphatic and aromatic amines to give the corresponding trimethylsilylamines and diphenylphosphine or dimethylphosphine respectively. These products were not isolated but were identified by comparing the values of their ^{1}H nmr chemical shifts and coupling constants with those values of the known compounds.

The reversibility of the exchange reaction was confirmed by the fact that dimethylamine and a silylphosphine could be identified as products when trimethylsilyldimethylamine was allowed to react with a phenylphosphine according to equation (2)

$$(2)\quad Me_3SiNMe_2 + HPPh_2 \longrightarrow Me_3SiPPh_2 + HNMe_2 .$$

Although these exchange processes favored the formation of the silylamine and phosphine, the reaction was shifted to

the right to favor the silylphosphine and dimethylamine by removing the volatile amine by distillation <u>in vacuo</u>.

The data for the equilibrium studies can be found in Tables XVI and XVII. In all the exchange reactions investigated in these studies, the substituents on silicon remained constant and the solvent was benzene. Thus, neither the effect of the groups on silicon nor the effect of the solvent on the reaction was determined.

The substituents on phosphorus and nitrogen were varied; therefore, the equilibrium constants could be determined as a function of the nature of the groups on these elements. The effects that the groups on nitrogen had on the position of equilibria in the reactions described by equation (1) for silylphosphines (I) and (II) were similar and will be discussed first. Of the factors which may be considered, we will focus our attention on two, the steric and electronic effects of the substituents on the amine. Primary aliphatic, secondary aliphatic and primary aromatic amines were used in the exchange reactions. For the aliphatic amines, the primary amines exchanged more completely than the secondary amines. Therefore, the steric effect is an important factor that appears to influence the position of equilibria. Factors that make the electron pair on nitrogen more available for $d\pi$-$p\pi$ bonding, such as the inductive effects of the alkyl amine groups or conjugative effects in substituted anilines may also influence the position of equilibria. Table XIX gives the basicity

Table XIX. Basicity constants of organic amines in water at 25^0 [67]

Amine	pKb	Kb
($\underline{iso}$-Pr)$_2$NH	1.95	1.1×10^{-3}
Et$_2$NH	3.02	9.6×10^{-4}
Me$_2$NH	3.28	5.2×10^{-4}
$\underline{tert}$-BuNH$_2$	3.55	2.8×10^{-4}
N-benzylmethylamine	4.42	3.8×10^{-5}
$\underline{p}$-toluidine	8.92	1.2×10^{-9}
$\underline{m}$-toluidine	9.31	4.9×10^{-10}
$\underline{o}$-toluidine	9.60	2.5×10^{-10}

constants for some amines in water. These constants represent the ability of the amine to donate their lone pair of electrons to hydrogen ions. Therefore, we assumed that the ability of amines to donate these electrons to d orbitals of silicon was proportional to the basicity of the amines. So, the stability of the silylamine should increase as the basicity of the amine increases. This effect, in turn should lead to the equilibria described in equation (1) being shifted to the right, and a higher value of the equilibrium constant should result. For the aliphatic amines, the secondary amines are more basic than the primary amines. According to basicity arguments, this would suggest that the secondary amines should exchange more completely than primary

amines. However, the reverse is true. For example, diisopropylamine is the most basic of the aliphatic amines but exchanged to a smaller extent than all others. These results are rationalized by suggesting that the steric nature of the amines influences the equilibrium constants to a greater extent than do the factors which make the electron pair on nitrogen more available for $d\pi$-$p\pi$ bonding.

The results from the equilibrium studies of the aromatic amines are more difficult to rationalize. The results from the equilibrium studies of the aliphatic amines suggested that the basicity of the amines influenced the position of equilibria only to a minor extent. Consequently, if only steric factors are considered, the values of the equilibrium constants for the primary aliphatic and aromatic amines should be similar because the steric nature of the two amines are similar (CH_3-  -NH_2 and $(CH_3)_3CNH_2$). However, the differences in the basicity between the aromatic and primary aliphatic amines

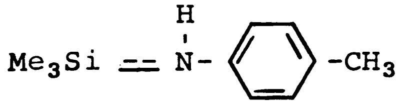
$$\frac{\text{Kb } \underline{\text{tert}}\text{-BuNH}_2}{\text{Kb } \underline{\text{p}}\text{-toluidine}} = \frac{2.8 \times 10^{-4}}{1.2 \times 10^{-9}} \approx 10^5$$

is greater than the difference in the basicity between the secondary and primary aliphatic amines

$$\frac{\text{Kb diisopropyl amine}}{\text{Kb } \underline{\text{tert}}\text{-BuNH}_2} = \frac{1.1 \times 10^{-3}}{2.8 \times 10^{-4}} < 10 \ .$$

Therefore, if basicity is a factor, the difference between the equilibrium constants obtained with primary aromatic and primary aliphatic amines should be greater than the

difference between the equilibrium constants obtained with two different aliphatic amines. Thus, if both basicity and steric factors are considered, the primary aliphatic amines would be expected to have larger values of the equilibrium constants than those of the aromatic amines. However, the values of the equilibrium constants for the aromatic amines are found to be approximately equal to those for the aliphatic amines (Kc for <u>tert</u>-BuNH$_2$ = 6.50, Kc for <u>p</u>-toluidine = 7.01). The values obtained may be attributed to the extra stability of the aromatic aminosilane compared to the primary aliphatic aminosilane from dπ-pπ contributions and the further stabilization of the Si-N bond in the aromatic aminosilane from the conjugation of this bond with the aromatic ring



.

This rationalization is based on the assumption that the Si-N bond in the aromatic aminosilanes does have some dπ-pπ character even though the lone pair of electrons on the aromatic amine has a smaller tendency to be donated to a silicon d orbital than does the lone pair of electrons on a primary aliphatic amine. The net effect of this conjugation is to apparently make the aromatic aminosilane as stable as the primary aliphatic aminosilane and in turn make the values of the equilibrium constants for the two amines equal.

The values of the equilibrium constants obtained for o-toluidine are low compared to those for the aromatic amines. This effect ("ortho effect") has been observed in the determination of the effect of substituents on the aromatic ring in aromatic acids and amines. This effect is not well understood but it has been suggested that it has to do with the nearness of the groups involved, but is more than just steric hindrance.[107]

The equilibrium constants are thermodynamic functions which reflect only the energies of the initial and final states; thus, the differences in the values of the equilibrium constants are due chiefly to differences in stabilities of the silylphosphines and the silylamines. In other words, the more stable the silylamines relative to the silylphosphines, the larger the values of the equilibrium constants for reaction described by equation (**1**). The change in the values of the equilibrium constants as a function of the change in the stability of the silylamines (keeping the stability of the silylphosphine constant) were discussed previously. The change in the equilibrium constants as a function of the change in the silylphosphine will now be discussed (the stability of the silylamine is held constant). A comparison of the values of the equilibrium constants in Table XVI to those in Table XVII shows that for any given amine the values of the equilibrium constants for the phenyl phosphinosilanes are larger than those for the methylphosphinosilanes. These results are

rationalized in the following manner: Obviously, the effects of the substituents on phosphorus are responsible for the different stabilities of the silylphosphines. The effect may be a steric factor or an electronic effect or both. Rationalizations based on steric effects appear to be in agreement with the experimental determinations of the values of the equilibrium constants. The phenyl groups are larger than the methyl groups; therefore, on the basis of steric effects it would be expected that the phenyl phosphinosilanes would be less stable than the methyl phosphinosilanes. Because the values of the equilibrium constants are larger in the case of the phenyl phosphinosilanes, arguments based on steric factors appear to be valid.

In order to determine the electronic effects of the substituents on phosphorus, the base strengths of the phophines must be determined. The ability of phosphorus to donate its electrons into d orbitals of silicon may be related to the basicity of the phosphine using arguments analogous to those employed in the discussion of π bonding of amines. The dissociation constants of some phosphines are listed in Table XX.[108]

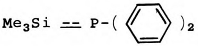
The table does not give the value of the pK for diphenylphosphine; however, it can be seen from the table that the methyl phosphines have larger pK values than the phenyl phosphines. Therefore, it may be reasonably assumed that dimethylphosphine has a larger pK value than diphenylphosphine. This conclusion about the basicity of

Table XX. Dissociation constants of some organic phosphines in ethanol-water mixtures

Phosphine	pK[a]
Me_3P	7.2
Et_3P	6.7
Me_2PhP	4.2
Et_2PhP	4.0
Ph_3P	2.6
Me_2PH	3.9

[a] $R_3PH^+ = R_3P + H^+$.

diphenylphosphine suggests that the dimethylphosphine group would favor donating its lone pair of electrons into d orbitals of silicon to a larger extent than the diphenylphosphine group. This factor by itself would cause the methylphosphinosilane to be more stable. But, if the Si-P bond in the methylphosphinosilane has π-bond character, it would be expected that the Si-P bond in the phenylphosphinosilane would also have π-bond character but to a lesser degree because the phenyl groups on phosphorus probably lower the ability of the phosphorus to donate its lone pair of electrons to the silicon d orbitals. Consequently, the Si-P π-bond in the phenyl phosphinosilanes would be conjugated with the aromatic rings attached to phosphorus



. This conjugation with the two

aromatic rings should stabilize the phenylphosphinosilanes compared to the methylphosphinosilanes. For example, the phenylaminosilane, Me_3SiN-  , was found to be much more stable from conjugative effects than the methylaminosilane, Me_3SiNMe_2.[67] Combining this electronic factor and the steric factor, the values for the equilibrium constants of the phenylphosphinosilanes should be smaller than those of methylphosphinosilanes. Or, in other words, the phenylphosphinosilanes should be more stable than the methylphosphinosilanes. The fact that the values of the equilibrium constants for the aromatic phosphinosilanes are larger rather than smaller than those for the methylphosphinosilanes suggested that $d\pi-p\pi$ bonding did not influence the relative stabilities of the two silylphosphines to a large extent. These conclusions about the lack of ability of phosphorus to donate its p electrons to empty d orbitals of silicon are also supported by other authors.[18, 21,22,23]

The values of the equilibrium constants for the reactions of trimethylsilyldimethylphosphine were also compared to those obtained for the reactions of trimethylsilyldimethylamine with other amines (Table III). Generally, the values of the equilibrium constants for the silylphosphines are larger than those for the silylamines. Also, the equilibria for the reaction of methylphosphinosilane with dimethylamine favors the formation of the methylaminosilane. These results suggested that the silylamines are more stable than the silylphosphines and also that the relative strength of the silicon-nitrogen bond is greater than that of the silicon-phosphorus bond. Although these results do not unequivocally negate $d\pi$-$p\pi$ bonding in silicon-phosphorus compounds, they may suggest that the silicon-phosphorus bond is not as stabilized by $d\pi$-$p\pi$ bonding as well as the silicon-nitrogen compounds.

The calculations in this investigation are based on the fact that the reactions described by equation (1) are in equilibrium. In order to establish the validity of the equilibrium constants determined for the forward reactions ($Me_3SiPR_2 + HNR'_2$), the values of the equilibrium constants were determined for the reverse reactions (see Table XVIII). The values obtained for these reverse reactions are in good agreement with those for the forward reactions, suggesting that the data is valid.

The results from the equilibrium studies which suggested that the lone pair of electrons on phosphorus in the silylphosphines were available for bonding motivated the study of the interaction of trimethylsilyldiphenylphosphine with nickel halides. This silylphosphine reacted with nickel iodide and nickel bromide under anhydrous conditions and at room temperature to give green solids. The formulas of these solids have been designated as $NiX_2[PPh_2SiMe_3]_2$ where X is Br or I. These solids were not obtained as pure products but as mixtures of $NiX_2[PPh_2SiMe_3]_2$ and $Ni(PPh_2)_2(PPh_2SiMe_3)_2$. The elemental analyses of these

solids suggested that the mixtures were predominately the $NiX_2(PPh_2SiMe_3)_2$ adducts. The $Ni(PPh_2)_2(PPh_2SiMe_3)_2$ was obtained from the cleavage of the silicon-phosphours bond by the nickel halide according to the following equation:

$$4Me_3SiPPh_2 + NiX_2 \longrightarrow 2Me_3SiX + Ni(PPh_2)_2(PPh_2SiMe_3)_2.$$

This nickel phosphide complex is very similar to the diamagnetic complex obtained by Issleib[104] by a similar reaction of NiX_2 with diphenylphosphine:

$$4HPPh_2 + NiX_2 \longrightarrow Ni(PPh_2)_2(HPPh_2)_2 + 2HX.$$

The reaction of the nickel halides with trimethylsilyldiphenylphosphine in benzene at about 86^0 gave predominately the previously described[101] complexes $NiX_2(HPPh_2)_{2 \text{ or } 3}$. The diphenylphosphine resulted from the hydrolysis of the ligand, Me_3SiPPh_2, by trace amounts of water.

The diphenylalkyl and triphenyl nickel halide complexes, $NiX_2(Ph_2PR)_2$, are paramagnetic and have been assigned in some cases tetrahedral structures.[102] However, the closely related complexes obtained in this investigation, $NiX_2(Ph_2PSiMe_3)$, where R is Me_3Si, are diamagnetic and their absorption spectra in benzene solution are consistent with square-planar structures. In particular, the complexes show no absorption bands near 900 mμ similar to those present in the paramagnetic complexes, $NiX_2(Ph_2PR)_2$. A closer examination of the magnetic susceptibility measurements for the diphenylalkyl complexes in benzene solutions

suggests that the magnetic moments are lower than expected for the presence of two unpaired electrons. This behavior was rationalized by first assuming that the intermediate values of the magnetic moments were due to the following equilibrium:

$$\underset{\text{Diamagnetic}}{(BuPh_2)_2NiX_2} \rightleftharpoons \underset{\text{Paramagnetic } (\mu_{eff} = 3.2\ \text{D.M.}).}{(BuPh_2)_2NiX_2}$$

If it is also assumed that the diamagnetic and paramagnetic species in benzene have square-planar structures, the magnetic susceptibility of the benzene solutions can be accounted for by postulating a diamagnetic ground state for the planar complex with an easily accesible paramagnetic excited state. Thus, if the separation between the two d orbitals of the metal (d_{xy} and $d_{x^2-y^2}$) is less than kT, an equilibrium as described above will arise. The fact that only diamagnetic species are observed for the complexes $NiX_2(PhP_2SiMe_3)_2$ suggests that the separation of the two d orbitals of the metal is larger than kT. This would dictate that the ligand, Me_3SiPPh_2, has greater ligand field strength than the Ph_2PR or Ph_3P ligands in order to increase the separation of the d orbitals above kT. It is suggested that the large inductive effect of the Me_3Si group compared to the alkyl groups is a possible explanation of the increase in field strength of the Me_3SiPPh_2 ligand over the $RPPh_2$ ligands. Thus, the square-planar diamagnetic structure of the $NiX_2(PPh_2SiMe_3)_2$ complexes can be rationalized.

SUMMARY

Trimethylsilylphosphines react with amines to give the corresponding trimethylsilylamine and phosphine. This is an equilibrium reaction which favors the formation of the silylamine over the silylphosphine.

The values of the equilibrium constants for these reactions, which were measured by ^{1}H nmr spectroscopy, varied with the substituents on the amine and phosphine. For a particular silylphosphine, the equilibrium constants were measured for reactions of the silylphosphine with secondary aliphatic, primary aliphatic and primary aromatic amines. The equilibrium constants for the reactions increased in the following order with respect to the amine: secondary aliphatic amines $<$ primary aliphatic amines $\lesssim$ primary aromatic amines. These results were rationalized by suggesting that both the steric nature of the amines and factors which make the electron pair on nitrogen more available for $d\pi$-$p\pi$ bonding are important and influence the values of the equilibrium constants. The steric factors influenced the values of the equilibrium constants of the aliphatic amines to a larger extent and the electronic factor was most important in influencing the values of the equilibrium constants of the aromatic amines.

The equilibrium constants for the reactions of a given amine with one of the two trimethylsilylphosphines Me_3SiPPh_2 or Me_3SiPMe_2, may be arranged in the following order, $Me_3SiPPh_2 < Me_3SiPMe_2$. The values of the equilibrium constants relative to the two silylphosphines were rationalized in terms of the size of the substituents on phosphorus (trimethylsilyldiphenylphosphine is sterically less stable than trimethylsilyldimethylphosphine).

The electronic factor which was expected to effect the equilibrium constants suggests that the silylphosphines are not stabilized by $d\pi$-$p\pi$ bonding to the same extent that the silylamines are stabilized by this type of interaction. Finally, the values of the equilibrium constants strongly support the fact that the relative strength of the silicon-nitrogen bond is greater than that of the silicon-phosphorus bond.

Complexes of the type NiL_2X_2 ($L = Me_3SiPPh_2$, $X = Br, I$) were obtained when trimethylsilyldiphenylphosphine was allowed to react with nickel halides. The complexes $NiX_2(HPPh_2)_2$ and $Ni(PPh_2)_2(PPh_2SiMe_3)_2$ were also obtained as products of this reaction. The $NiX_2(HPPh_2)_2$ resulted from the hydrolysis of the ligand, Me_3SiPPh_2, and the $Ni(PPh_2)_2(Me_3SiPPh_2)_2$ resulted from the cleavage of the Si-P bond in Me_3SiPPh_2.

In contrast to the paramagnetic tetrahedral or <u>cis</u>-square-planar structure of most $NiX_2(RPPh_2)_2$ complexes, the $NiX_2(Me_3SiPPh_2)_2$ has been assigned a diamagnetic square-

planar structure. The difference between the two complexes have been assigned to the greater ligand field strength of the Me_3SiPPh_2 ligand compared to the $RPPh_2$ ligand which in turn has been related to the larger positive inductive effect of the Me_3Si- group.

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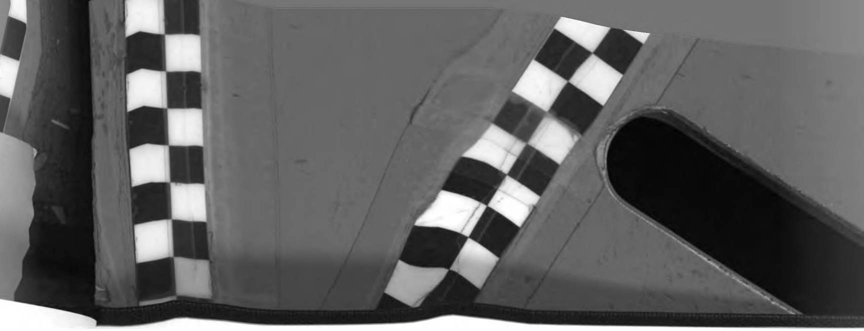

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APPENDIX I

INFRARED SPECTRA OF COMPOUNDS

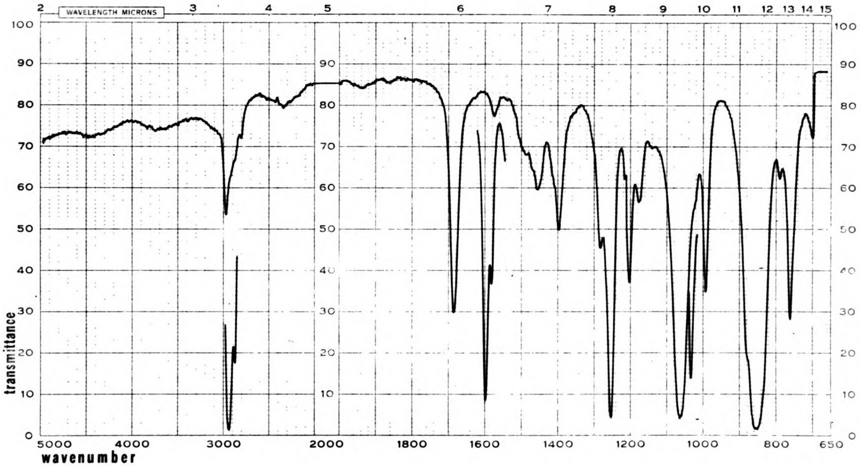


Figure 1. Infrared spectrum of trimethylsilyldimethylamine.

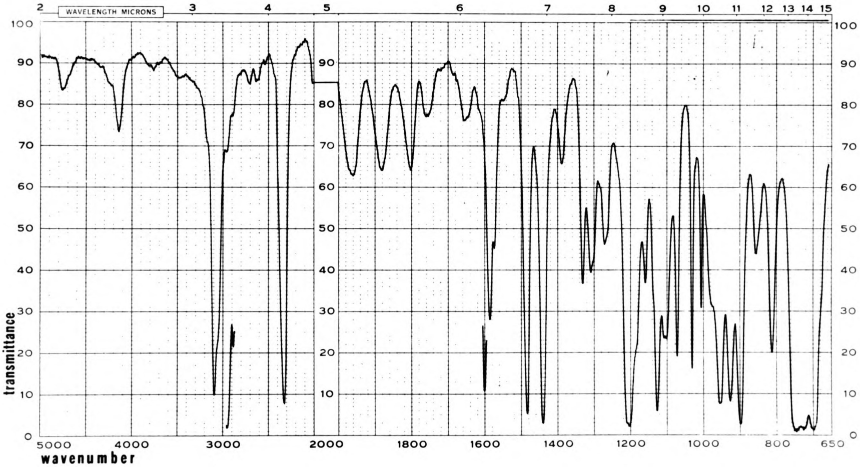


Figure 2. Infrared spectrum of diphenylphosphine.

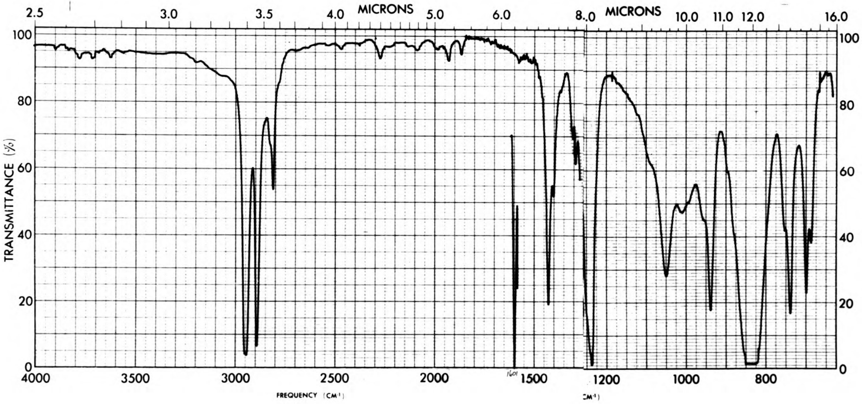


Figure 3. Infrared spectrum of trimethylsilyldimethylphosphine.

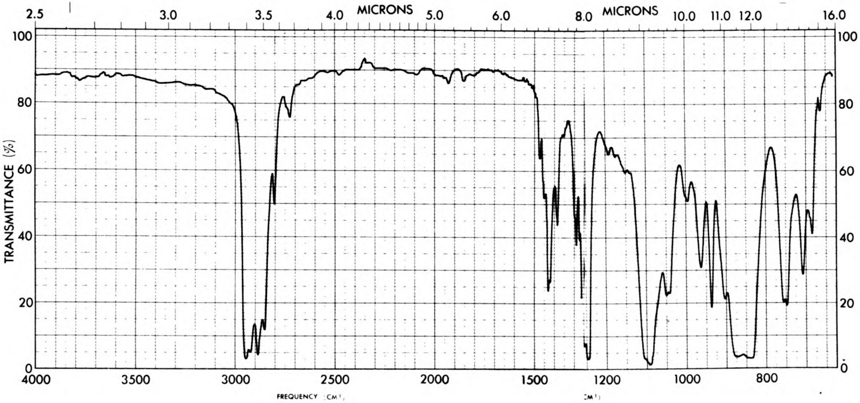


Figure 4. Infrared spectrum of the product from the cleavage of tetrahydrofuran.

APPENDIX II

PROTON NMR SPECTRA OF COMPOUNDS

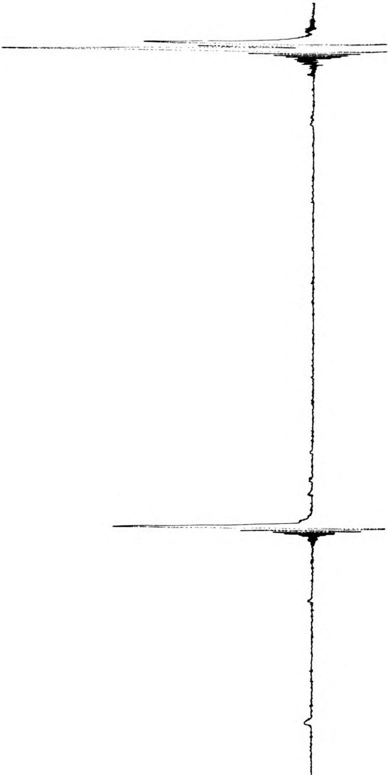


Figure 1. ^1H nmr spectrum of trimethylsilyldimethylamine.

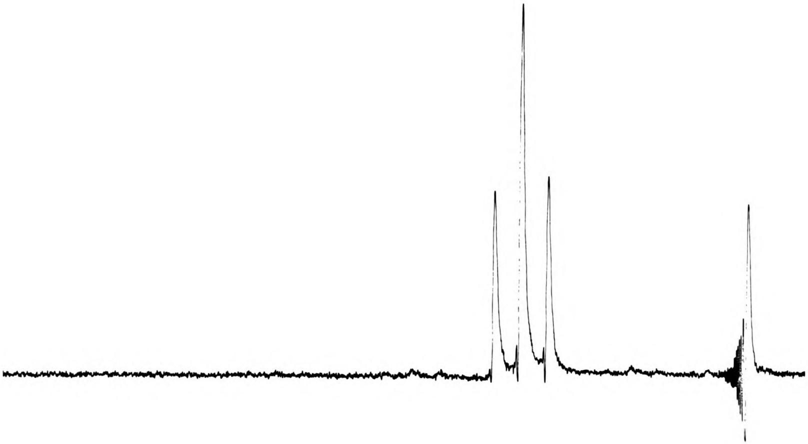


Figure 2. ^{1}H nmr spectrum of tetramethyldiphosphine.

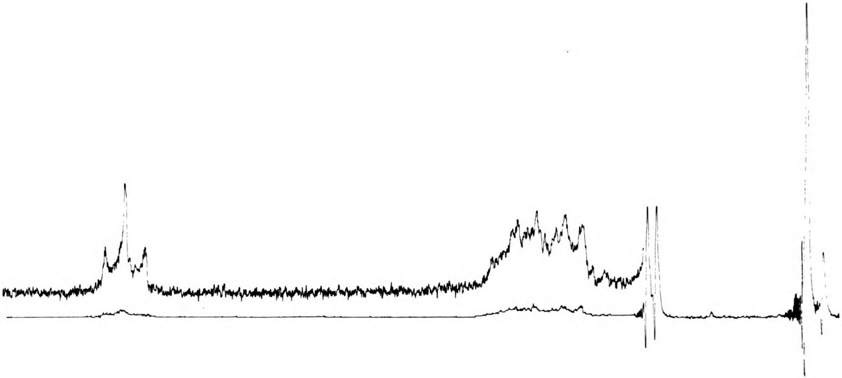
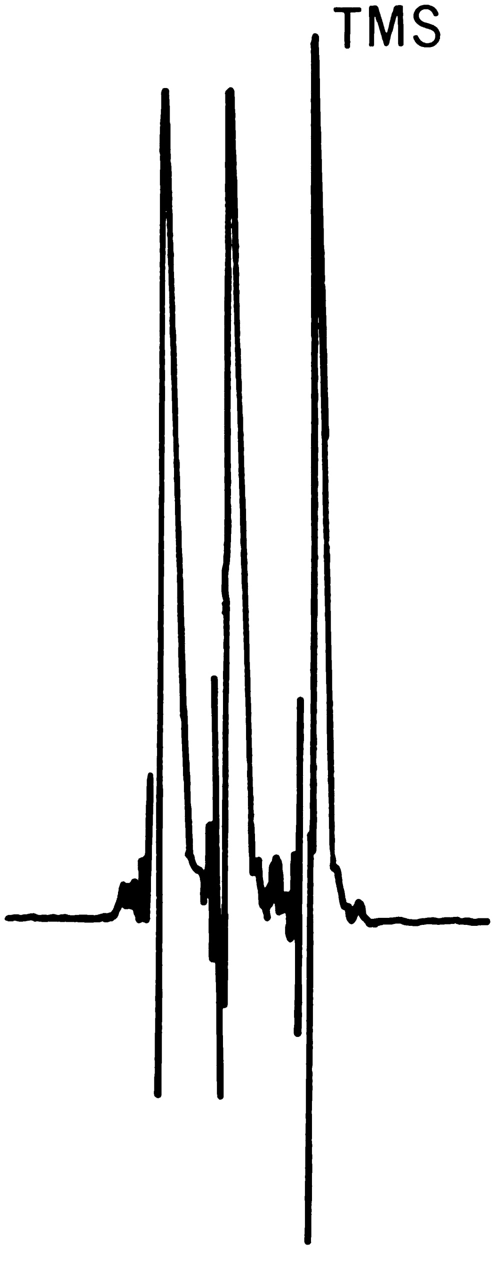


Figure 4. ^1H nmr spectrum of the product from the cleavage of tetrahydrofuran with lithium dimethylphosphide.

Figure 5.

^{1}H nmr SPECTRUM OF Me_3SiPPh_2



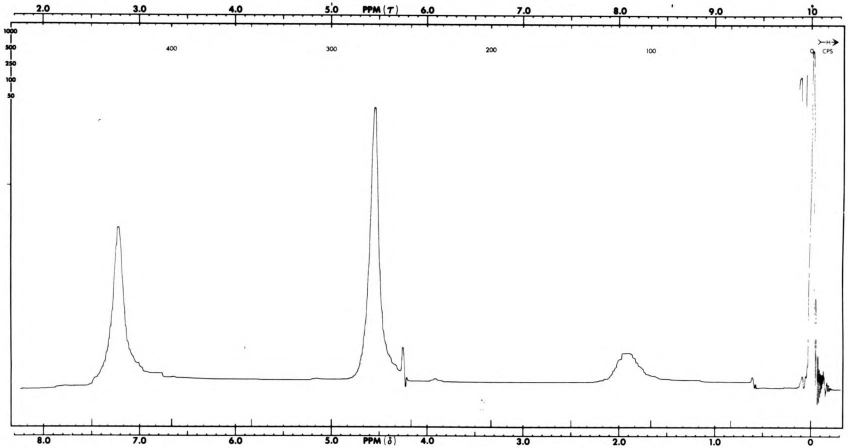


Figure 6. ^1H nmr spectrum of N-methylbenzylamine.

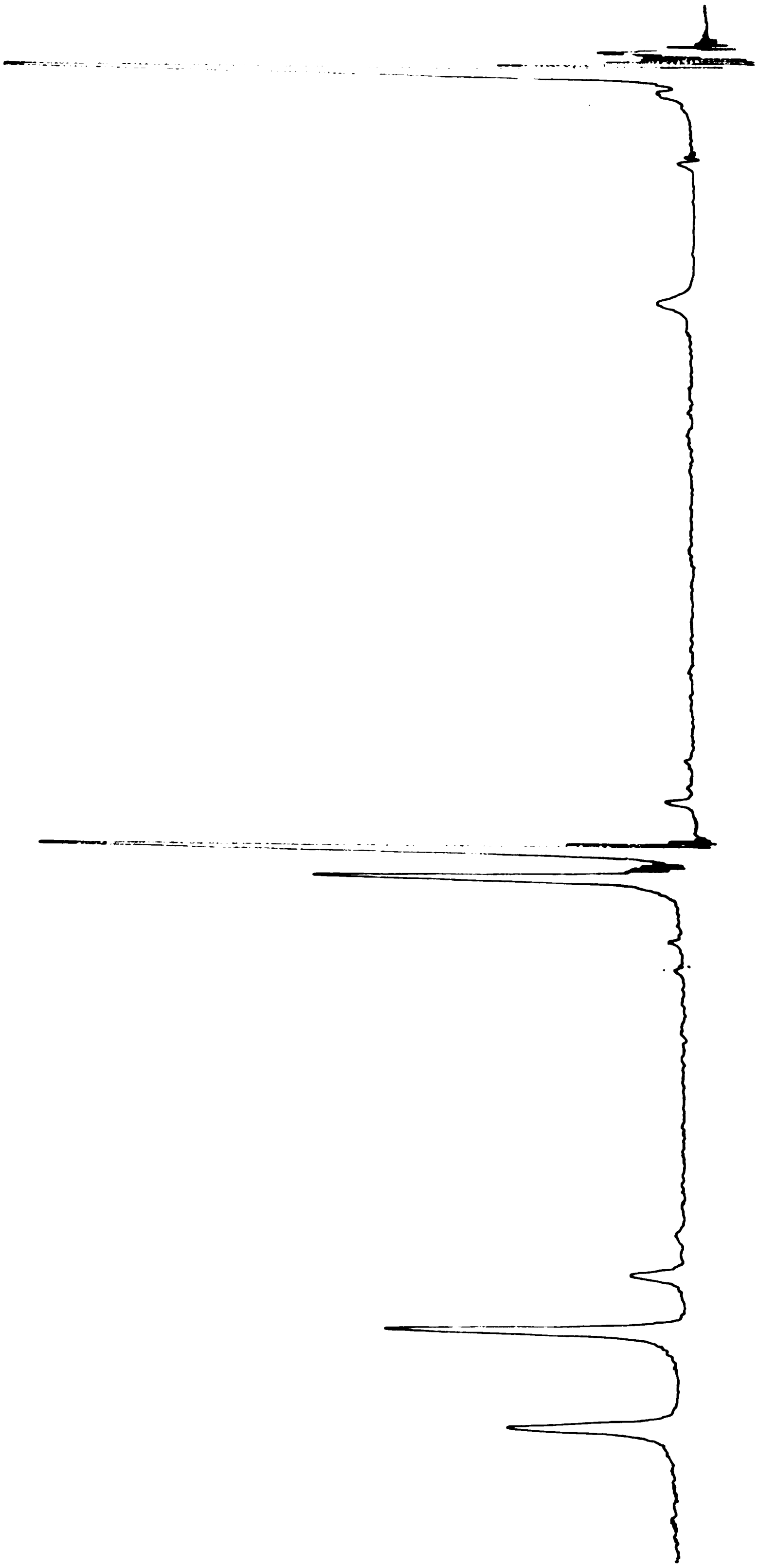


Figure 7. ^{1}H nmr spectrum of the equilibrium mixture from the reaction of trimethylsilyldiphenylphosphine with N-methylbenzylamine.

Figure 8. ^{1}H nmr spectrum of the equilibrium mixture from the reaction of dimethylamine with trimethylsilyldiphenylphosphine.

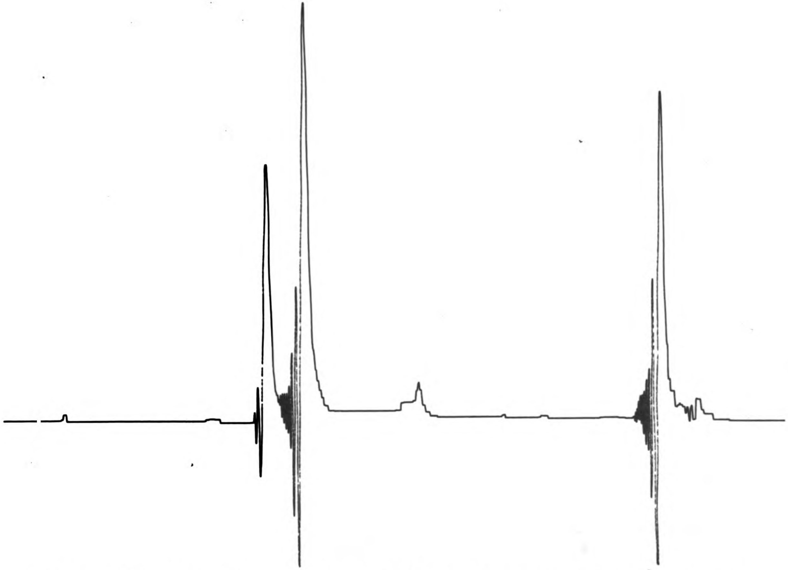


Figure 9. ^1H nmr spectrum of the equilibrium mixture from the reaction of <u>tert</u>-butylamine with trimethylsilyldiphenylphosphine.

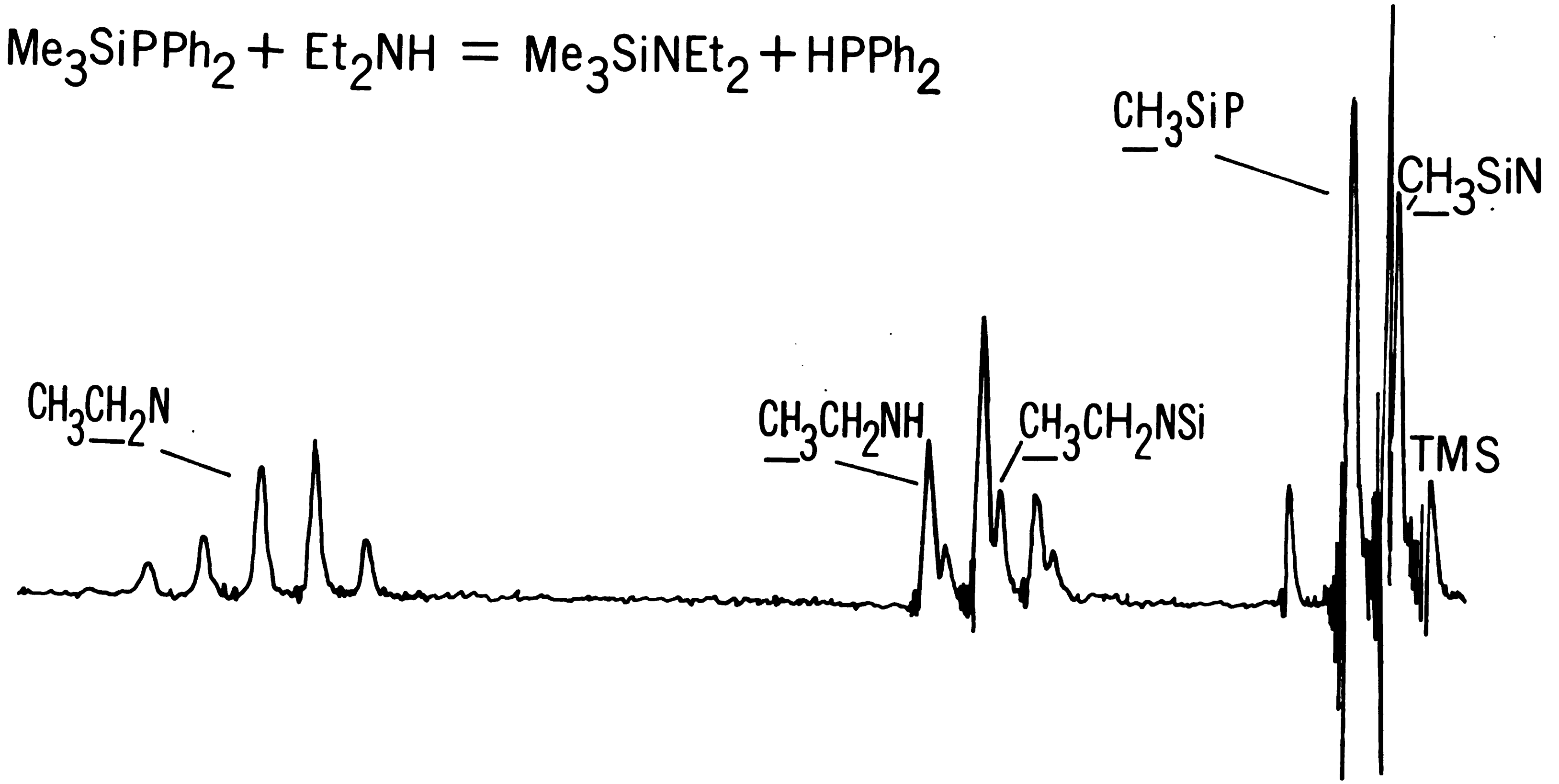


Figure 10. ^{1}H nmr spectrum of the equilibrium mixture from the reaction of diethylamine with trimethylsilyldiphenylphosphine.

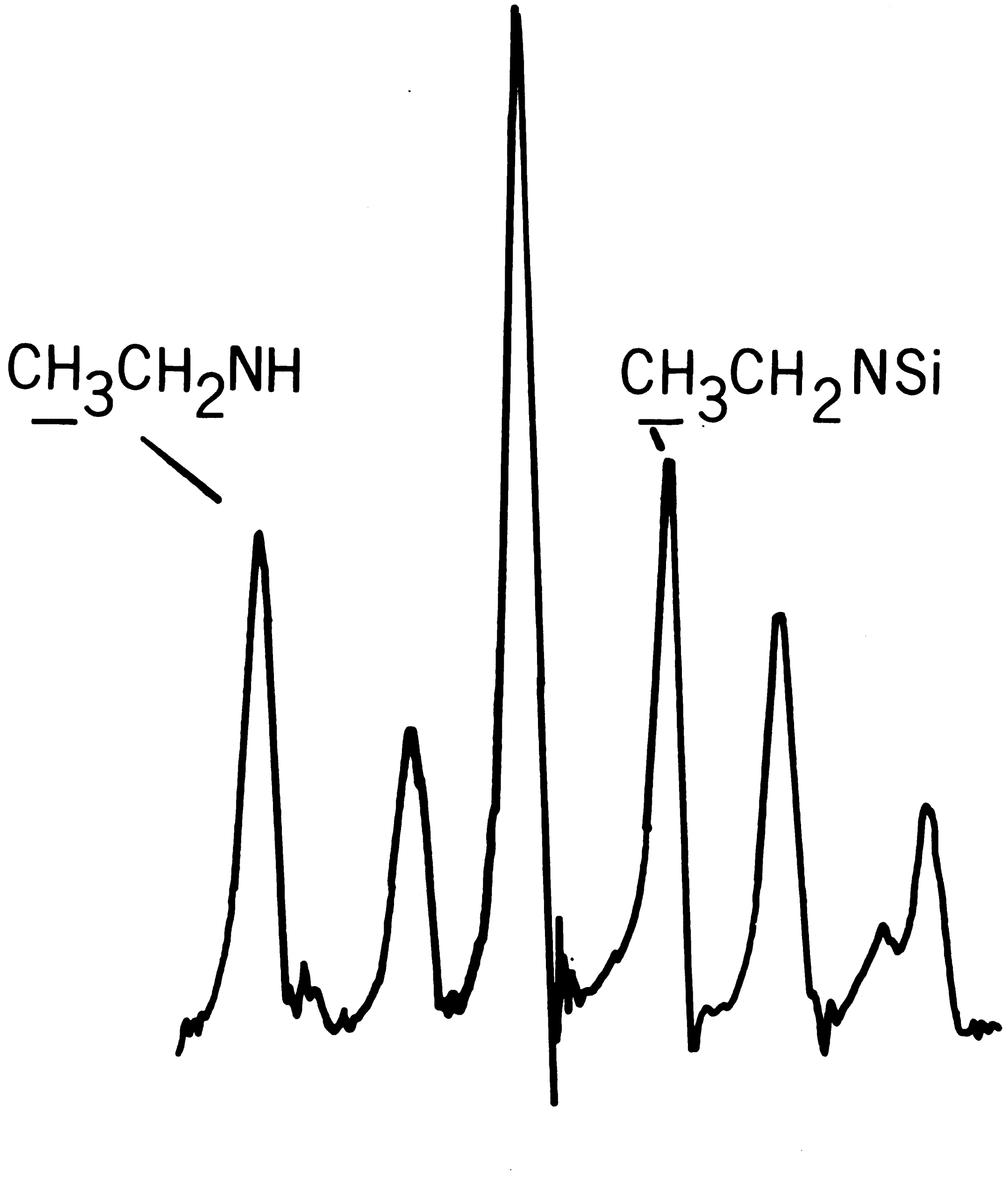


Figure 11. ^1H nmr spectrum of the equilibrium mixture from the reaction of diethylamine with trimethylsilyldiphenylphosphine (100 Mc).