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The synthesis of the N-silylphosphoranimines [e.g., \( \text{Me_2SiN=P[(OCH_3)CF_3]} \)] undergoes a variety of reactions including deprotonation/substitution of the P=Me groups, transilylation, and condensation with reactive phosphines. Some new 1,2-addition and oxidation reactions of the P-C systems, \( R_2\text{NP=CHR}, \) \( R_2\text{NP}(-\text{NR})=\text{CHR} \), and \( R_2\text{NP=CR-CH=CHR} (R = \text{SiMe}_3) \), are also reported.

Keywords:
Silylated Phosphines and Phosphoranimines

by


Prepared for Publication in Phosphorus and Sulfur

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October 10, 1986

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SILYLATED PHOSPHINES AND PHOSPHORANIMINES

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Abstract: The N-silylphosphoranimines [e.g., Me_3SiN=P(OCH_2CF_3)Me_2] undergo a variety of reactions including deprotonation/substitution of the P-Me groups, transilylation, and condensation with reactive phosphines. Some new 1,2-addition and oxidation reactions of the P=C systems, R_2NP=CHR, R_2NP(-NR)=CHR, and R_2NP=CR-CH=CHR (R = SiMe_3) are also reported.

The chemistry of compounds containing Si-N-P and/or Si-C-P linkages is usually markedly different from that of the nonsilylated analogues. On the one hand, the Si-N or Si-C bonds may function as reactive sites so that processes such as transilylation and condensation reactions via silane elimination are commonly found. Alternatively, the steric and electronic properties of the silyl groups can impart both kinetic stability and interesting chemical reactivity to a variety of low-coordinate phosphorus systems. We report here several illustrative examples of these principles.

REACTIONS OF N-SILYLPHOSPHORANIMINES

Various P-functionalized N-silylphosphoranimines are useful precursors to cyclic and polymeric phosphazenes. Recently, the synthetic utility of such compounds has
been greatly expanded through two general types of
reactions. First, deprotonation/silylation of the P-
methyl group followed by a Peterson olefination affords
a series of vinyl derivatives (eq 1). Some of these

\[
\begin{align*}
\text{Me} & \quad \text{(1) n-BuLi} & \quad \text{Me} \\
\text{Me}_3\text{SiN} &= \text{POCH}_2\text{CF}_3 & \text{Me}_3\text{SiN} &= \text{POCH}_2\text{CF}_3 \\
\text{Me} & \quad \text{(2) Me}_3\text{SiCl} & \quad \text{Me} & \quad \text{Me}_3\text{SiCl}
\end{align*}
\]

(1)

(2)

(3)

R_2\text{C(O)} = \text{Me}_2\text{C(O)}, \text{PhC(O)H}, \text{PhC(O)Me}, \text{PhC(O)CF}_3,
\text{PhC(O)CH=CH}_2, \text{Me}_2\text{C=CH-C(O)-CH=CMe}_2

"monomers" undergo condensation polymerization to yield
poly(phosphazenes) bearing substituted C=C side groups.

Second, we have studied a broad spectrum of Si-N
bond cleavage reactions. For example, transilylation
processes yield a series of novel N-silylphosphoran-
imines (eq 2) bearing reactive substituents on silicon
as well as some bis(phosphoraniminosilanes and
-siloxanes (eq 3). The related reactions involving
cleavage of the Si-N bond in Me_3SiN=P(X)Me_2 [X = Cl, Br,
OCH_2CF_3, and N(SiMe_3)_2] by reactive phosphines, e.g.,
Ph_2PY (Y = Cl, OCH_2CF_3), are generally more complex.

\[
\begin{align*}
\text{CF}_3\text{CH}_2\text{O} &\quad \text{RSiMe}_2\text{Cl} &\quad \text{CF}_3\text{CH}_2\text{O} \\
\text{Me}_3\text{SiN} &= \text{PMe}_2 &\quad \text{RMe}_2\text{SiN} &= \text{PMe}_2
\end{align*}
\]

(2)

R = Ph, CH=CH_2, Cl, (CH_2)_3CN, CH_2CH_2C(O)Me,
SiMe_2(CH_2)_2SiMe_2Cl
\[
\begin{align*}
CF_3CH_2O + ECl_2 & \rightarrow CF_3CH_2O \\
2 Me_3SiN=PMe_2 & \rightarrow [Me_2P=N]_2E \\
\end{align*}
\]

(3)

\[
E = SiMe_2, SiMe_2(CH_2)_2SiMe_2, Me_2Si(OSiMe_2)_n \\
n = 1-5
\]

These reactions occur with elimination of Me_3SiY and, depending upon the choice of reactants, lead to various open-chain ionic species (e.g., A and B).

\[
\begin{align*}
[Ph_2P-P=N-P-X]^+ Cl^- & \quad [Ph_2P-P=N-P-N=P-PPh_2]^+ Cl^- \\
Ph Me & \quad Ph Me Ph \\
Ph Me & \quad Ph R Ph
\end{align*}
\]

A: X = Cl, Br, OCH_2CF_3
B: R = Me, Ph

Surprisingly, the permethylated analogue of A (X = OCH_2CF_3) is produced in high yield in the "transilylation" of Me_2SiHCl with Me_3SiN=P(OCH_2CF_3)Me_2.

**REATIONS OF SILYLATED P=C COMPOUNDS**

In this area our recent work has included a comparative study of the reactivity of the P=C bonds in the analogous P(III) and P(V) compounds, (Me_3Si)_2NP=CHSiMe_3 and (Me_3Si)_2NP(NSiMe_3)=CHSiMe_3, respectively. In general, the 1,2-addition of polar reagents to the P=C bond occurs more readily in the P(V) system. For example, while the former does not react with PhPCl_2, the latter undergoes Si-N cleavage and ring formation (eq 4) subsequent to the 1,2-addition process. Some reagents, on the other hand, react smoothly with both substrates. Cyclopentadiene, for example, affords a Diels-Alder adduct in each case.
A stable, acyclic 1-phosphadiene has also been prepared (eq 5) and we have begun to investigate its derivative chemistry. Interestingly, simple oxidation reactions (e.g., with sulfur or Me₃SiN₃) are accompanied by isomerization to four-membered ring products (eq 6). In the sulfur reaction, a three-membered disulfide ring, (Me₃Si)₂NP(S)-S-C(SiMe₃)CH=CHSiMe₃ is also produced.

**ACKNOWLEDGEMENTS**

This research is generously supported by the U.S. Army Research Office, the U.S. Office of Naval Research, and the Robert A. Welch Foundation.
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