AD-A118 005 TEXAS CHRISTIAN UNIV FORT WORTH DEPT OF CHEMISTRY F/G 7/3
SYNTHESIS AND STEREOCHEMISTRY OF SOME (SILYLAMINO)PHOSPHINIMINE--ETC(U)
AUG 82 R H NEILSON, J S ENGENITO N00014-79-C-0632
UNCLASSIFIED TR-82-01 NL

1 OF 1
AD
A118005

END
DATE
FILMED
09-82
DTIC

(12)

OFFICE OF NAVAL RESEARCH
Contract N00014-79-C-0632
Task No. NR 053-720
TECHNICAL REPORT NO. 82-01

Synthesis and Stereochemistry of Some (Silylamino)phosphinimines

by

Robert H. Neilson and Joseph S. Engenito, Jr.

Prepared for Publication

in

Organometallics

Texas Christian University
Dept. of Chemistry
Fort Worth, TX 76129

August 1, 1982

Unclassified
SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE

READ INSTRUCTIONS
BEFORE COMPLETING FORM

1. REPORT NUMBER
82-01

2. GOVT ACCESSION NO.
AD-A118005

3. RECIPIENT'S CATALOG NUMBER

4. TITLE (and Subtitle)
Synthesis and Stereochemistry of
Some (Silylamino)phosphinimines

5. TYPE OF REPORT & PERIOD COVERED
Technical Report 1981

6. PERFORMING ORG. REPORT NUMBER
TR-82-01

7. AUTHOR(s)
R.H. Neilson and J. S. Engenito, Jr.

8. CONTRACT OR GRANT NUMBER(s)
N00014-79-C-0632

9. PERFORMING ORGANIZATION NAME AND ADDRESS
Texas Christian University
Fort Worth, TX 76129

10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
NR-053-720

11. CONTROLLING OFFICE NAME AND ADDRESS
Office of Naval Research

12. REPORT DATE

13. NUMBER OF PAGES
18

14. MONITORING AGENCY NAME & ADDRESS(if different from Controlling Office)

15. SECURITY CLASS. (of this report)

15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

Approved for public release: distribution unlimited

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

Prepared for publication in Organometallics

18. SUPPLEMENTARY NOTES

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Phosphinimine
Dynamic NMR
Silylamino phosphine

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

A series of P-alkyl-P-halo substituted (silylamino)phosphinimines $(Me_3Si)_2N-P(R)X=NSiMe_3$ are obtained either by oxidative addition of RI (R = Et, *i*-Pr, *t*-Bu) to $(Me_3Si)_2N-P=NSiMe_3$ or by treatment of $[(Me_3Si)_2N]_2PMe$ with I_2 or Br_2. Reaction of the iodophosphinimines with MeLi affords the

DD FORM 1 JAN 73 1473 EDITION OF 1 NOV 65 IS OBSOLETE
S/N 0102-LF-014-6601

Unclassified
SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

20. ABSTRACT

dialkyl derivatives $(Me_3Si)_2N$-P(R)Me=$NSiMe_3$ (R = Et, i-Pr, t-Bu). Alcoholysis of the t-BuI product in the presence of Et_3N yields the N-H compounds Me_3SiN(H)-P(t-Bu)OR=$NSiMe_3$ (R = Me, CH_2CF_3). Variable-temperature ^1H NMR studies of these (silylamino)phosphinimines demonstrate that, depending on what substituents are present, they may be fluxional via [1,3]-silyl exchange, hindered rotation about the amino P-N bond, or [1,3]-proton exchange. The results are discussed in terms of the electronic and steric effects of the phosphorus substituents.

Contribution from the
Department of Chemistry
Texas Christian University
Fort Worth, TX 76129

Synthesis and Stereochemistry of Some (Silylamino)phosphinimines

ROBERT H. NEILSON* and JOSEPH S. ENGENITO, Jr.

Received ______________

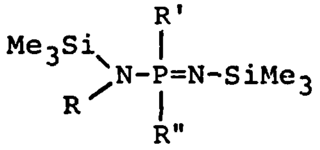
Abstract

- A series of P-alkyl-P-halo substituted (silylamino)phosphinimines $(Me_3Si)_2N-P(R)X=NSiMe_3$ are obtained either by oxidative addition of RI (R = Et, i-Pr, t-Bu) to $(Me_3Si)_2N-P=NSiMe_3$ or by treatment of $[(Me_3Si)_2N]_2PMe$ with I_2 or Br_2. Reaction of the iodophosphinimines with MeLi affords the dialkyl derivatives $(Me_3Si)_2N-P(R)Me=NSiMe_3$ (R = Et, i-Pr, t-Bu). Alcoholysis of the t-BuI product in the presence of Et_3N yields the N-H compounds $Me_3SiN(H)-P(t\text{-}Bu)OR=NSiMe_3$ (R = Me, CH_2CF_3). Variable-temperature ^1H NMR studies of these (silylamino)phosphinimines demonstrate that, depending on what substituents are present, they may be fluxional via [1,3]-silyl exchange, hindered rotation about the amino P-N bond, or [1,3]-proton exchange. The results are discussed in terms of the electronic and steric effects of the phosphorus substituents.

Introduction

Several recent studies have focused on the preparative chemistry and dynamic stereochemistry of compounds containing the Si-N-P linkage. For example, their importance as polyphosphazene precursors[1,2] is now well established and their use in organophosphorus[3-5] and organometallic chemistry[6-8] is beginning to develop. Investigations of stereochemical features of these compounds, including P-N bond rotation[9,10] and silyl group rearrangements,[11-15] have also been conducted and it is these areas to which this paper is most relevant.

We report here the synthesis and dynamic NMR study of a series of (silylamino)phosphinimines of general formula:

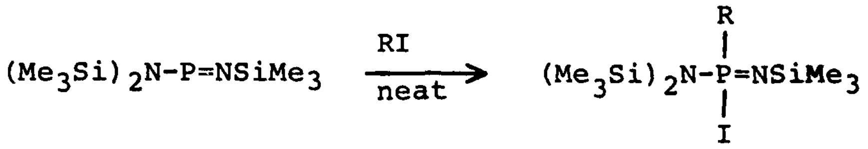


$$(\mathrm{Me_3Si})(\mathrm{R})\mathrm{N{-}P(R')(R'')}{=}\mathrm{N{-}SiMe_3}$$

Depending on what substituents are present, it is possible to observe any of three stereochemical processes: (1) [1,3]-silyl exchange, (2) [1,3]-proton exchange if R=H, and (3) hindered rotation about the amino P-N bond.

Results and Discussion

Synthesis. Treatment of the 2-coordinate compound [bis(trimethylsilylamino)](trimethylsilylimino)phosphine (**1**)[16,17] with one equivalent of an alkyl iodide (*except MeI*) results in the rapid and quantitative formation of the 4-coordinate oxidative addition product **2** (eq 1). These phosphinimines (**2**) are yellow,



$$(Me_3Si)_2N\text{-}P\text{=}NSiMe_3 \xrightarrow[\text{neat}]{RI} (Me_3Si)_2N\text{-}\overset{R}{\underset{I}{P}}\text{=}NSiMe_3 \qquad (1)$$

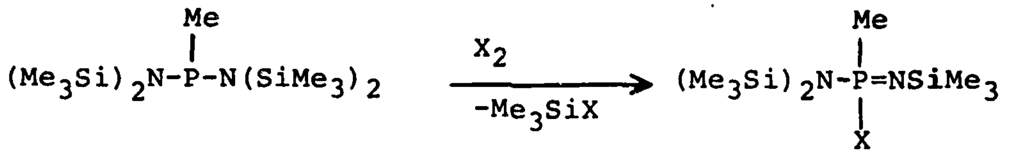
1

2a, R = t-Bu
2b, R = i-Pr
2c, R = Et

moisture-sensitive liquids of marginal thermal stability. As reported by Niecke,[18] the ethyl compound **2c** can be distilled under reduced pressure without decomposition. The more sterically crowded compounds **2a** and **2b**, which are reported here for the first time, however, decompose rapidly on heating with elimination of Me_3SiI and formation of unidentified solid products. The characterization of these compounds, therefore, is based on NMR spectroscopy (Table I) and their derivative chemistry (see below).

Rather surprisingly, the analogous reaction with MeI is very slow and is incomplete even after stirring for 2 weeks. Analysis by NMR spectroscopy indicates the formation of a complex mixture of products. Qualitative observations indicate that the relative rate of the reaction increases markedly as the steric bulk of the alkyl group increases. This suggests that attack by the phosphine on iodine of RI with possible carbonium ion (R^+) formation may be an operative reaction pathway.

The iodomethane adduct **2d** and its bromine analogue **4** were prepared by the direct halogenation (eg 2) of the bis(amino)phosphine **3**[19]. We have previously reported a similar type of reaction



$$(Me_3Si)_2N-\overset{Me}{P}-N(SiMe_3)_2 \xrightarrow[-Me_3SiX]{X_2} (Me_3Si)_2N-\underset{X}{\overset{Me}{P}}=NSiMe_3 \qquad (2)$$

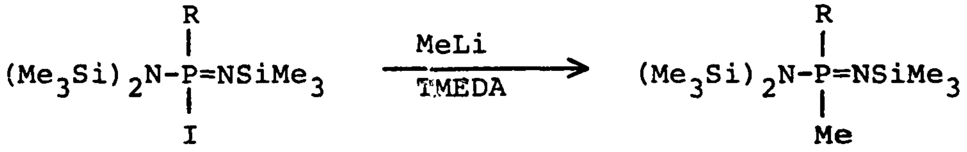
3

2d, X = I

4, X = Br

for the simple (silylamino)phosphines $(Me_3Si)_2NPR_2$.[20] Both of these P-methyl derivatives were colorless liquids that could be distilled with no evidence of decomposition, indicating that the thermal stability of such compounds is enhanced by the presence of less bulky alkyl substituents.

The P-iodophosphinimines 2a-2c were readily converted to the P-methyl derivatives 5a-5c by treatment with methyllithium in ether with activation by TMEDA (eq 3). The dimethyl analogue $(Me_3Si)_2N-PMe_2=NSiMe_3$ (5d), prepared by a Staudinger reaction of $(Me_3Si)_2NPMe_2$, has



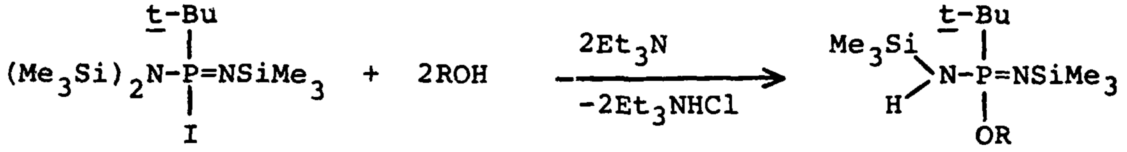
$$(Me_3Si)_2N-\underset{I}{\overset{R}{P}}=NSiMe_3 \xrightarrow[TMEDA]{MeLi} (Me_3Si)_2N-\underset{Me}{\overset{R}{P}}=NSiMe_3 \qquad (3)$$

2

5a, R = t-Bu
5b, R = i-Pr
5c, R = Et

been previously reported.[21] These dialkylphosphinimines are colorless liquids which were readily purified by vacuum distillation and characterized by NMR and elemental analysis (Tables I and II).

Attempts to prepare other derivatives of the P-iodophosphinimines generally gave unsatisfactory results. Dehydrohalogenation reactions of 2 with amines or alcohols resulted in complex mixtures. The N-H phosphinimines **6a** and **6b** were the only characterized products obtained in low yields (*ca*. 15%) from the reactions of **2a** with alcohols (eg 4). The use of just one equivalent of the alcohol gave essentially the same results.



(4)

2a

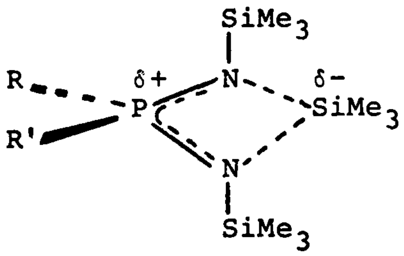
6a, R = Me

6b, R = CH_2CF_3

Stereochemistry. Dynamic ^1H NMR studies of these new (silylamino)-phosphinimines provide evidence for at least three distinct stereochemical processes: (1) [1,3]-silyl exchange, (2) hindered rotation about the amino P-N bond, and (3) [1,3]-proton exchange. The results obtained from these experiments are summarized in Table III.

The phenomenon of reversible [1,3] silyl exchange is common to all of the trisilylated compounds (i.e. **2a-d**, **4**, **5a-d**). For example, the ^1H NMR spectrum of **2b** shows the two signals (in a 2:1 intensity ratio) expected for the Me_3Si protons. At higher temperatures the [1,3]-silyl shift becomes rapid, leading to coalescence of the signals and permitting an estimate of the exchange barrier $\Delta G^{\ddagger}_{1,3}$. For **2b** the process can also be monitored qualitatively by observing diastereotopic methyl groups within the *i*-propyl moiety. When the [1,3]-silyl exchange is rapid, the phosphorus chirality is lost and the *i*-propyl methyl groups become equivalent. The silyl exchange process is thought to be intramolecular since, within experimental error, the same results are obtained whether the compound is studied neat or in solution.

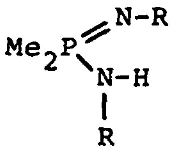
The $\Delta G^{\ddagger}_{1,3}$ values (Table III) all lie within the fairly narrow range of ca. 13.5-18.5 kcal/mole. Similar results have been reported previously for a few related compounds.[12] It is noted that the dialkylphosphinimines 5 generally have exchange barriers which are 3-4 kcal/mole lower than the corresponding alkyl(halo)phosphinimines 2 and 4. This trend is consistent with our earlier observation[12] that electron-releasing groups (e.g. Me) on phosphorus reduce the [1,3]-silyl exchange barrier. This can be rationalized as an inductive effect whereby electron-releasing substituents tend to increase the nucleophilicity of the imino nitrogen, thus facilitating its attack on the amino-$SiMe_3$ group. Moreover, alkyl groups should tend to stabilize the positive charge on phosphorus which develops in the likely transition state species.



The steric bulk of the substituents on phosphorus seems to have less of an affect on the $\Delta G^{\ddagger}_{1,3}$ values. For example, the results for the individual dialkyl compounds 5 differ by only ca. 1 kcal/mole, suggesting that the size of the groups on phosphorus does not play a dominant role in this process. An explanation is lacking at this time, however, for the low $\Delta G^{\ddagger}_{1,3}$ value of **2a**. Studies of compounds containing *two* bulky groups on phosphorus are needed before a more definitive conclusion about steric effects can be made.

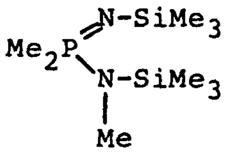
Perhaps more significant than the [1,3]-silyl exchange is the additional observation of hindered rotation about the *amino* P-N bond in some of these phosphinimines. Compound **2a**, for instance, exibits three distinct Me_3Si signals of equal intensity at *ca*. -70°C. As the temperature is raised, two of the signals broaden and coalesce at -54°C giving two peaks in a 2:1 intensity ratio. At 18°C a second coalescence point is observed, finally resulting in the single broad peak which is seen at room temperature. These results clearly show that two separate fluxional processes are operative here: (1) [1,3]-silyl exchange at higher temperatures (large $\Delta G^{\ddagger}$ value) and (2) restricted $P\text{-}N(SiMe_3)_2$ rotation at low temperatures (smaller $\Delta G^{\ddagger}$ value). This conclusion is also consistent with the fact that we were able to measure P-N rotation barriers only for the most sterically congested compounds (**2a**, **2b**, and **5a**). The general trend of $\Delta G^{\ddagger}_{PN}$ values increasing with the size of the phosphorus substituents is well documented.[22]

Still a third type of dynamic stereochemical process appears to be occurring in the disilylated N-H compounds **6a** and **6b**. The Me_3Si groups in **6a**, for example, appear as a single peak at room temperature but as two signals of equal intensity at temperatures below *ca*. -40°C. This fluxional behavior could be attributed to either [1,3]-silyl exchange as above or to [1,3]-proton exchange. Previous studies have shown that the non-silylated phosphinimines **7** are, in fact, fluxional at room temperature[23], presumably via [1,3]-proton exchange; whereas, the disilyl(alkyl)phosphinimine **8** is not fluxional.[12] The combination of these results strongly suggests that [1,3]-proton exchange is



R = Me, *t*-Bu

7



8

the more likely of the two pathways for compounds **6a** and **6b**. Once again, it is noted that the compound with the more electron-releasing substituent (i.e. OMe in **6a**) has the lower barrier to the rearrangement process.

Experimental Section

Materials and General Procedures. The following reagents were obtained from commercial sources and used without purification: iodoalkanes, methanol, 2,2,2-trifluoroethanol, bromine, iodine, TMEDA, triethylamine, and methyllithium (ether solution). Benzene and ether were distilled from CaH_2 prior to use; other solvents were dried over molecular sieves. The iminophosphine $(Me_3Si)_2N\text{-}P{=}NSiMe_3$ (**1**)[17] and the P,P-dimethylphosphinimine **5d**[21] were prepared and purified according to published procedures. Bis[bis(trimethylsilyl)-amino](methyl)phosphine (**3**) was prepared by a modification of the Wilburn method;[11,24] full details of the synthesis and characterization of **3** will be reported as part of another study.[25] Proton NMR spectra were recorded on a Varian EM-390 spectrometer; ^{13}C and ^{31}P NMR, both with ^1H decoupling, were obtained in the FT mode on a JEOL FX-60 instrument. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, N.Y.

All reactions and other manipulations were carried out under an atmosphere of dry nitrogen or under vacuum. The procedures described herein are typical of those used for the preparation of new compounds in this study.

P-bis(trimethylsilyl)amino-P-*tert*-butyl-P-iodo-N-(trimethylsilyl)-phosphinimine, 2a. The iminophosphine **1** (18.80 g, 67.5 mmol) was weighed under N_2 in a 50-mL flask which was then equipped with a magnetic stirrer and an adapter with a N_2-inlet side arm and a rubber septum. The flask was cooled to 0°C and *t*-butyl iodide (8.04 mL, 67.5 mmol) was added via syringe. The mixture was warmed to room temperature and stirred for 2 h. Iodotrimethylsilane was removed under vacuum and identified by comparison of its ^1H NMR to that of an authentic sample. Nearly a quantitative yield of phosphinimine **2a** remained as a viscous yellow liquid of good purity based on NMR data (Table II). Attempted distillation (bath temperature *ca*. 130°C) under vacuum resulted in decomposition with Me_3SiI evolution and formation of unidentified yellow solids. The composition of **2a** was further confirmed by the preparation of its stable P-methyl derivative **5a**.

The analogous compounds **2b** and **2c** were prepared by the same procedure except that longer reaction times (*ca*. 18-24 h) were required. As reported by Niecke,[18] the ethyl derivative **2c** could be distilled (bp 112-115°C/0.2 mm) without decomposition.

P-bis(trimethylsilyl)amino-P-iodo-P-methyl-N-(trimethylsilyl)phosphinimine, 2d. Asolution of iodine (*ca*. 4.6 g, 18 mmol) in benzene (60 mL) was added dropwise to a stirred solution of the bis(amino)phosphine **3**[25] (6.01 g, 16.4 mmol) in benzene (30 mL) at 0°C. This titration-like addition was stopped when a faint orange color of iodine persisted in the solution. The mixture was then stirred for 90 min at room temperature before benzene and Me_3SiI were removed under vacuum. Distillation afforded **2d** as a pale yellow liquid which crystallized on standing (Tables I and II). An identical procedure using bromine gave the analogous P-bromophosphinimine **4** as a colorless liquid.

P-bis(trimethylsilyl)amino-P-*tert*-butyl-P-methyl-N-(trimethylsilyl)phosphinimine, 5a. Methyllithium (22.6 mL, 1.4 M in Et_2O) was added with stirring to a solution of **2a** (13.95 g, 30.2 mmol; freshly prepared as described above) in Et_2O (100 mL) at 0°C. After *ca*. 30 min, no formation of LiCl was evident so TMEDA (4.78 mL, 31.7 mmol) was added to accelerate the reaction. The mixture was warmed to room temperature and stirred overnight. After filtration under nitrogen and solvent removal under reduced pressure, distillation afforded **5a** as a colorless liquid (Tables I and II). The same procedure was used to prepare compounds **5b** and **5c**.

P-*tert*-butyl-P-methoxy-P-(trimethylsilyl)amino-N-(trimethylsilyl)phosphinimine, 6a. A 500 mL, 3-necked flask, equipped with an addition funnel and a paddle stirrer, was charged with the iodophosphinimine **2a** (13.09 g, 28.3 mmol), Et_2O (150mL), and Et_3N (7.9 mL, 56.6 mmol). The mixture was cooled to 0°C and a solution of methanol (2.3 ml, 56.6 mmol) in Et_2O (50 ml) was added dropwise. Immediate precipitation of Et_3NHI was observed. The mixture was then warmed to room temperature and stirred overnight. Filtration under nitrogen and solvent removal under reduced pressure gave a cloudy, viscous liquid residue. Distillation gave a major fraction (*ca.* 5 mL, bp 65-70 °C/0.2 mm) which contained 6a and other unidentified products. Redistillation afforded a pure sample of 6a as a colorless liquid (Tables I and II). Compound 6b was prepared by the same procedure from 2a and CF_3CH_2OH.

Dynamic NMR Spectra. All spectra were recorded on the Varian EM-390 instrument equipped with a standard Varian temperature controller. Temperatures were regulated to an estimated ±2 °C and were calibrated against methanol and ethylene glycol reference samples. The no-exchange chemical shift difference $\Delta\nu$ and the coalescence temperature T_c were determined from the spectra. The $\Delta G^\ddagger$ values were calculated[26] by the so-called approximate method[27] which has been shown to give accurate results when applied to such two-site exchange processes.[28] The data are summarized in Table III. Values of $\Delta G^\ddagger$ measured for the same compound in different solvents never differed by more than 0.5 kcal/mole.

Acknowledgement. We thank the Office of Naval Research and the Robert A. Welch Foundation for generous financial support of this research.

References and Notes

1. Wisian-Neilson, P.; Neilson, R.H. *J. Am. Chem. Soc.* **1980**, *102*, 2848.
2. Wisian-Neilson, P.; Neilson, R.H. *J. Macromol. Sci. Chem.* **1981**, *A16*, 425.
3. Neilson, R.H. *Inorg. Chem.* **1981**, *20*, 1679.
4. Morton, D.W.; Neilson, R.H. *Organometallics* **1982**, *1*, 289.
5. Morton, D.W.; Neilson, R.H. *Organometallics* **1982**, *1*, 623.
6. Scherer, O.J.; Jungmann, H. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 953.
7. Keim, W.; Appel, R.; Storeck, A.; Kruger, C.; Goddard, R. *Angew. Chem., Int. Ed. Engl.* **1981**, *20* 116.
8. Scherer, O.J.; Konrad, R.; Kruger, C.; Tsay, Yi-H. *Chem. Ber.* **1982**, *115*, 414.
9. Neilson, R.H.; Lee, R. C.-Y; Cowley, A.H. *Inorg. Chem.* **1977**, *16*, 1455.
10. Scherer, O.J.; Puttmann, M. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 679.
11. Wilburn, J.C.; Neilson, R.H. *Inorg. Chem.* **1979**, *18*, 347.
12. Wilburn, J.C.; Wisian-Neilson, P.; Neilson, R.H. *Inorg. Chem.* **1979**, *18*, 1429.
13. Neilson, R.H.; Wisian-Neilson, P.; Wilburn, J.C. *Inorg. Chem.* **1980**, *19*, 413.
14. Glidewell, C. *J. Organomet. Chem.* **1976**, *108*, 335.
15. Hodgson, P.K.G.; Katz, R.; Zon, G. *J. Organomet. Chem.* **1976**, *117*, C63.
16. Niecke, E.; Flick, W. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 585.
17. Scherer, O.J.; Kuhn, N. *Angew. Chem., Int. Ed. Engl.* **1974**, *13*, 811.
18. Niecke, E., Bitter, W. *Chem. Ber.* **1976**, *109*, 415.
19. See Experimental Section.
20. Wisian-Neilson, P.; Neilson, R.H. *Inorg. Chem.* **1980**, *19*, 1875.
21. Wilburn, J.C.; Neilson, R.H. *Inorg. Chem.* **1977**, *16*, 2519.
22. See reference 9 and papers cited therein.
23. Scherer, O.J.; Schnabl, G.; Lenhard, Th. *Z. Anorg. Allg. Chem.* **1979**, *449*, 167.

24. Neilson, R.H.; Wisian-Neilson, P. *Inorg. Chem.* in press.

25. Manuscript in preparation.

26. The equation $\Delta G^{\ddagger} = Tc[45.67 + 4.58 \log(Tc/\Delta\nu)]$ gives $\Delta G^{\ddagger}$ in cal/mol with Tc in ^{o}K. See Neilson, R.H.; Wells, R.L. *Inorg. Chem.* **1977**, *16*, 7.

27. Gutowsky, H.S.; Holm, C.H. *J. Chem. Phys.*, **1956**, *25*, 1228.

28. Kost, D.; Carlson, E.H.; Raban, M. *Chem. Commun.* **1971**, 656.

Table I. NMR Spectroscopic Data[a]

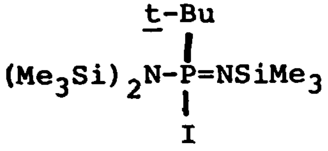
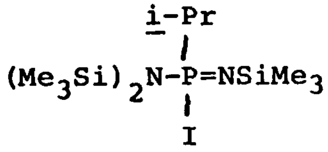
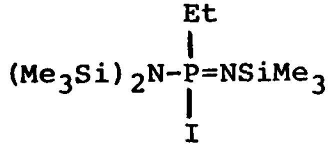
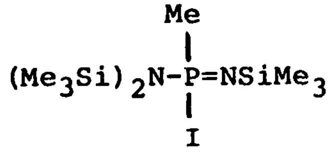
		^1H NMR		^{13}C NMR		^{31}P NMR
compd	signal	δ	J_{PH}	δ	J_{PC}	δ
 $(Me_3Si)_2N\text{-}P(t\text{-}Bu)(I)\text{=}NSiMe_3$ 2a	Me_3Si	0.35[b]		6.90		7.73
	$\underline{Me}_3C$	1.18	22.5	26.18	2.4	
	$Me_3\underline{C}$			46.35	92.2	
 $(Me_3Si)_2N\text{-}P(i\text{-}Pr)(I)\text{=}NSiMe_3$ 2b	$(Me_3Si)_2N$	0.48		5.28	2.4	-0.81
	Me_3SiN	0.12	0.4	2.72	4.9	
	$PCH\underline{Me}_2$	1.12[c]	21.0	14.88	5.5	
		1.22	27.6	17.46		
	$P\underline{CH}Me_2$	2.58	9.3	42.54	90.9	
 $(Me_3Si)_2N\text{-}P(Et)(I)\text{=}NSiMe_3$ 2c	$(Me_3Si)_2N$	0.48		5.03	2.4	-10.72
	Me_3SiN	0.12		2.01	5.5	
	$PCH_2\underline{Me}$	1.08	24.3	7.41	7.9	
	$P\underline{CH_2}Me$	2.50[d]		42.48	87.9	
 $(Me_3Si)_2N\text{-}P(Me)(I)\text{=}NSiMe_3$ 2d	$(Me_3Si)_2N$	0.38		5.08	2.4	-27.04
	Me_3SiN	0.07		1.89	5.5	
	PMe	2.30	15.0	37.79	89.7	

Table I. continued

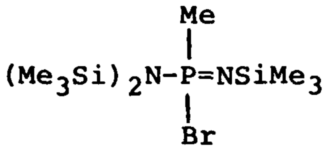
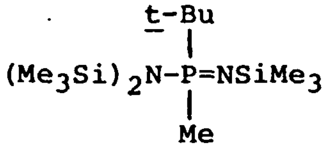
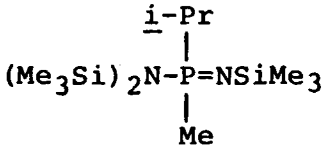
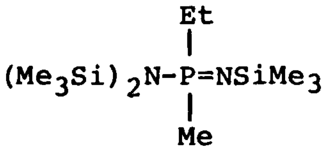
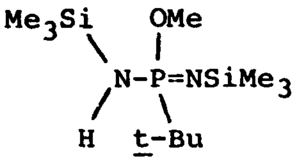
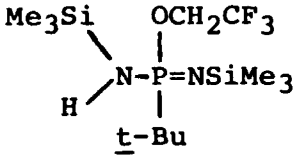
compd	signal	^1H NMR		^{13}C NMR		^{31}P NMR
		δ	J_{PH}	δ	J_{PC}	δ
 $(Me_3Si)_2N-\overset{Me}{\underset{Br}{P}}=NSiMe_3$ 4	$(Me_3Si)_2N$	0.40		5.16	2.4	2.63
	Me_3SiN	0.08		2.60	4.9	
	PMe	2.12	15.6	33.75	100.1	
 $(Me_3Si)_2N-\overset{\underline{t}\text{-}Bu}{\underset{Me}{P}}=NSiMe_3$ 5a	Me_3Si	0.38[b]		5.93		30.15
	$\underline{Me}_3C$	1.24	15.5	26.56	2.5	
	$Me_3\underline{C}$			36.24	88.5	
	PMe	1.54	11.3	19.27	62.9	
 $(Me_3Si)_2N-\overset{\underline{i}\text{-}Pr}{\underset{Me}{P}}=NSiMe_3$ 5b	Me_3Si	0.26[b]		5.60		25.07
	$PCH\underline{Me}_2$	1.08[e]	17.4	16.08		
	$P\underline{CH}Me_2$	1.86	7.0	31.76	85.4	
	PMe	1.45	12.0	21.16	68.4	
 $(Me_3Si)_2N-\overset{Et}{\underset{Me}{P}}=NSiMe_3$ 5c	Me_3Si	0.31[b]		5.32		21.10
	$PCH_2\underline{Me}$	1.16	18.0	6.22	4.9	
	$P\underline{CH_2}Me$	1.72[f]		29.36	79.4	
	PMe	1.52	12.3	23.07	72.0	

Table I. continued

compd	signal	^1H NMR δ	^1H NMR J_{PH}	^{13}C NMR δ	^{13}C NMR J_{PC}	^{31}P NMR δ
 6a	Me_3Si	0.10[b]		2.96		25.15
	$\underline{Me_3}C$	1.04	15.9	25.58		
	$Me_3\underline{C}$			33.16	127.6	
	OMe	3.42	11.6	49.22	7.3	
	NH	1.60				
 6b	Me_3SiNH	0.07		2.19		24.67
	Me_3SiN	0.24		3.65		
	$\underline{Me_3}C$	1.13	16.8	25.30		
	$Me_3\underline{C}$			33.57	125.1	
	OCH_2	4.10[g]	7.5	59.39[h]	6.7	
	CF_3			124.20[h]	9.8	
	NH	1.83				

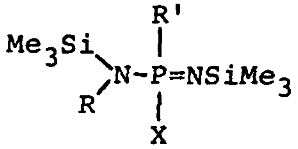
[a] Chemical Shifts downfield from Me_4Si for ^1H and ^{13}C spectra and from H_3PO_4 for ^{31}P spectra; coupling constants in Hz. Solvents: ^1H, CH_2Cl_2; ^{13}C and ^{31}P, $CDCl_3$. [b] Exchange-broadened singlet. [c] $J_{HH} = 7.2$ Hz. [d] Complex multiplet, $J_{HH} \sim 7.5$ Hz. [e] $J_{HH} = 7.0$ Hz. [f] Broad unresolved multiplet. [g] $J_{FH} = 8.7$ Hz. [h] $J_{FCC} = 36.6$ Hz; $J_{FC} = 277.7$ Hz.

Table II. Preparative and Analytical Data for New Phosphinimines

compd	preparative		analytical[a]	
	% yield	bp, °C (mm)	% C	%H
2d	43	90-91 (0.1)[b]	28.69 (28.56)	7.26 (7.19)
4	69	68-70 (0.04)[c]	32.32 (32.16)	8.11 (8.10)
5a	54	82-84 (0.08)	47.93 (47.95)	11.09 (11.21)
5b	32	81-82 (0.04)	46.23 (46.38)	11.26 (11.08)
5c	39	64-65 (0.08)	44.69 (44.67)	11.06 (10.93)
6a	16	43-44 (0.05)	45.03 (44.86)	10.76 (10.61)
6b	14	61-62 (0.9)	39.81 (39.76)	8.43 (8.34)

[a] Calculated values in parentheses. [b] Solid, mp 48-50°C.
[c] Solid, mp 27-32°C.

Table III. Variable-Temperature ^{1}H NMR Data[a] for (Silylamino)phosphinimines,



$Me_3Si(R)N-P(R')(X)=NSiMe_3$

[1,3]-silyl exchange

compd	R	R'	X	solvent	Tc (°C)	Δν (Hz)	ΔG‡ (kcal/mole)
2a	Me_3Si	t-Bu	I	CH_2Cl_2	12	33.6	14.2
2b	Me_3Si	i-Pr	I	neat	97	30.6	18.7
				anisole	90	26.0	18.5
2c	Me_3Si	Et	I	neat	60	30.6	16.8
				anisole	51	24.0	16.5
2d	Me_3Si	Me	I	neat	72	34.8	17.3
4	Me_3Si	Me	Br	neat	77	34.2	17.6
5a	Me_3Si	t-Bu	Me	CH_2Cl_2	18	19.8	14.8
5b	Me_3Si	i-Pr	Me	CH_2Cl_2	15	28.2	14.5
5c	Me_3Si	Et	Me	CH_2Cl_2	-3	28.8	13.5
5d	Me_3Si	Me	Me	CH_2Cl_2	-3	28.8	13.5
P-N(R)SiMe$_3$ rotation							
2a	Me_3Si	t-Bu	I	CH_2Cl_2	-12	6.2	13.9
2b	Me_3Si	i-Pr	I	CH_2Cl_2	-74	5.1	10.6
5a	Me_3Si	t-Bu	Me	CH_2Cl_2	-54	29.1	10.8
[1,3]-proton exchange							
6a	H	t-Bu	OMe	CH_2Cl_2	-40	16.8	11.9
6b	H	t-Bu	OCH_2CF_3	CH_2Cl_2	>45	15.3	>16.4

[a] Estimated experimental uncertainties in ΔG‡ are ±0.5 kcal/mole