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Synthesis and Carbon Tetrachloride Reactions of Bis[bis(trimethylsilyl)amino]phosphines[1]

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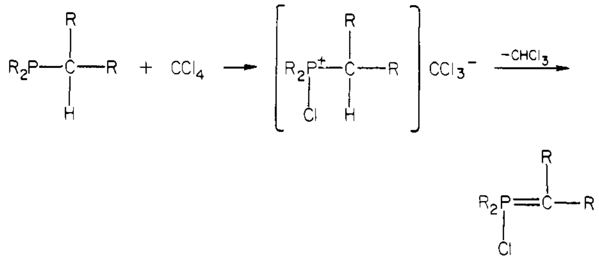
The bis(disilylamino)phosphines $[(Me_3Si)_2N]_2PCH_2R$ (**1**, R = H; **2**, R = Me; **3**, R = $SiMe_3$; **4**, R = Ph) were prepared from the reactions of the appropriate Grignard reagents with $[(Me_3Si)_2N]_2PCl$. Compound **5**, $[(Me_3Si)_2N]_2PCH(Ph)SiMe_3$, was prepared from $[(Me_3Si)_2N]_2PCl$ and the TMEDA complex of $Me_3SiCH(Li)Ph$. Compound **1** reacted with Me_3SiN_3 to give $[(Me_3Si)_2N]_2P(Me){=}NSiMe_3$ (**6**) and with MeI to give $[(Me_3Si)_2N]_2PMe_2{}^+I^-$ (**7**). Treatment of **7** with alkyllithium reagents afforded $(Me_3Si)_2NPMe_2{=}NSiMe_3$ (**8**) and $(Me_3Si)_2NPMe(CH_2SiMe_3){=}NSiMe_3$ (**9**). The reactions of **1**–**4** with CCl_4 gave mixtures of $(Me_3Si)_2NPCl(Me_3SiCHR){=}NSiMe_3$ (**10**) and $(Me_3Si)_2NPCl(CH_2R){=}NSiMe_3$ (**11**). When the CCl_4 reactions were done neat, **10** was the major product, while **11** predominated when the reactions were carried out in CH_2Cl_2 solution. Compound **5** reacted with CCl_4 to give only $(Me_3Si)_2NPCl(Me_3SiCHPh){=}NSiMe_3$ (**10d**).

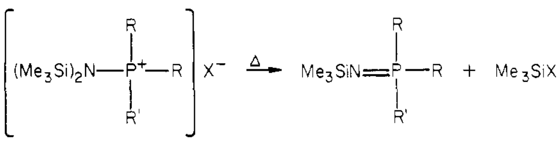
Introduction

The chemistry of (disilylamino)phosphines, e.g. $(Me_3Si)_2NPMe_2$, has proven to be quite diverse as a result of the reactivity of the silicon–nitrogen bond combined with the nucleophilicity of phosphorus.[2] Much less is known, however, about the chemistry of phosphines bearing two disilylamino substituents. The thermally unstable chloro-substituted phosphine $[(Me_3Si)_2N]_2PCl$ is an important precursor to novel two-coordinate phosphorus species including the iminophosphine $(Me_3Si)_2NP{=}NSiMe_3$,[3] the phosphenium ion $[(Me_3Si)_2N]_2P^+$,[4] and the free radical $[(Me_3Si)_2N]_2P\cdot$.[5] We were interested in preparing alkyl-substituted phosphines with two disilylamino groups, $[(Me_3Si)_2N]_2PR$, in order to assess their stability as well as their reactivity compared to those of related mono(disilylamino)phosphines.

The reaction of these bis(disilylamino)phosphines with CCl_4 was of particular interest since two reaction pathways and, hence, two different types of products seemed possible. It is well established that an ion-pair intermediate R_3PCl^+,CCl_3^- is formed on initial interaction of CCl_4 with tertiary phosphines.[6] In systems containing a proton α to phosphorus, the CCl_3^- anion can abstract the proton to form phosphorus ylides (eq 1).[7] When silylamino groups are present, however, proton abstraction might compete with silicon–nitrogen bond cleavage. Precedent for such cleavage has been observed for several related disilylamino-substituted phosphonium salts (eq 2).[8]



$$R_2P-\overset{R}{\underset{H}{C}}-R + CCl_4 \rightarrow \left[R_2\underset{Cl}{P^+}-\overset{R}{\underset{H}{C}}-R\right]CCl_3^- \xrightarrow{-CHCl_3} R_2\underset{Cl}{P}=\overset{R}{C}-R \quad (1)$$



$$\left[(Me_3Si)_2N-\overset{R}{\underset{R'}{P^+}}-R\right]X^- \xrightarrow{\Delta} Me_3SiN=\overset{R}{\underset{R'}{P}}-R + Me_3SiX \quad (2)$$

We have, therefore, prepared a series of stable bis(disilylamino)phosphines $[(Me_3Si)_2N]_2PR$ and have investigated the reaction of these new phosphines with CCl_4. Depending on the reaction conditions employed, both pathways discussed above were found to be operative.

Results and Discussion

Phosphine Synthesis. The new bis(disilylamino)phosphines $[(Me_3Si)_2N]_2PCH_2R$, where R = H, Me, $SiMe_3$, and Ph, were prepared by treating $[(Me_3Si)_2N]_2PCl$[3] with the appropriate Grignard reagent (eq 3). Due to its thermal instability

$$2LiN(SiMe_3)_2 + PCl_3 \rightarrow [(Me_3Si)_2N]_2PCl \xrightarrow{RCH_2MgX} [(Me_3Si)_2N]_2PCH_2R \quad (3)$$

1, R = H
2, R = Me
3, R = $SiMe_3$
4, R = Ph

$[(Me_3Si)_2N]_2PCl$ was purified only by filtration to remove LiCl; the Grignard reagents were then added to the filtrate. The phosphine products **1**–**4** were purified by vacuum distil-

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(1) Wisian-Neilson, P.; Ford, R. R.; Li, B.-L.; Neilson, R. H. "Abstracts of Papers", 183rd National Meeting of the American Chemical Society, Las Vegas, NV, March 1982; American Chemical Society: Washington, DC, 1982; INORG 147.

(2) Morton, D. W.; Neilson, R. H. *Organometallics* **1982**, *1*, 289 and references cited therein.

(3) Scherer, O. J.; Kuhn, N. *Angew. Chem., Int. Ed. Engl.* **1974**, *13*, 811.

(4) Cowley, A. H.; Lattman, M.; Wilburn, J. C. *Inorg. Chem.* **1981**, *20*, 2916.

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(6) Appel, R. *Angew Chem., Int. Ed. Engl.* **1975**, *14*, 801.

(7) (a) Appel, R.; Peters, J.; Schmitz, R. *Z. Anorg. Allg. Chem.* **1981**, *18*, 475. (b) Kolodiazhnyi, O. I. *Tetrahedron Lett.* **1980**, *21*, 3983.

(8) (a) Morton, D. W.; Neilson, R. H. *Organometallics* **1982**, *1*, 623. (b) Wilburn, J. C. Ph.D. Dissertation, Duke University, Durham, NC, 1978.

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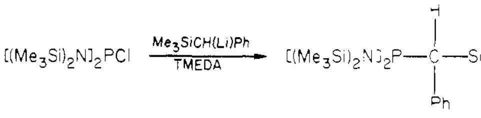
Table I. Preparative and Analytical Data

	preparative		analytical[a]	
compd	% yield	bp, °C (*P*, mm)	% C	% H
1	64	97-100 (0.05)	42.30 (42.57)	10.70 (10.72)
2	64	98-99 (0.05)	43.91 (44.16)	10.73 (10.85)
3	50	135-140 (0.2)	44.08 (43.74)	10.93 (10.70)
4	39	158 (0.2)	51.27 (51.48)[e]	9.72 (9.71)
5	35	mp 175-180	48.76 (51.26)	9.54 (9.90)
6	71	105 (0.03)	42.38 (42.30)	10.35 (10.65)
9	21	72-73 (0.02)	44.34 (44.16)	10.80 (10.85)
10a	87[b]	90-100 (0.03)	see **11c**	
10b	47[b]	115-123 (0.07)	40.20 (40.50)	9.73 (9.64)
10c	63[b]	120-123 (0.1)	40.28 (40.56)	9.56 (9.74)
10d	40[b] (95)[d]	124 (0.02)	47.86 (47.76)	9.01 (8.80)
11a	72[c]	77-78 (0.1)	36.25 (36.46)	9.02 (9.11)
11b	86[c]	61 (0.02)	38.49 (38.51)	9.60 (9.40)
11c	77[c]	100-108 (0.29)	38.90 (38.88)	9.47 (9.47)
11d	71[c]	94-97 (0.02)	47.48 (47.39)	8.26 (8.39)

[a] Calculated values in parentheses. [b] From neat CCl_4 reaction. [c] From CCl_4 reaction in CH_2Cl_2. [d] From the reaction of **5** with CCl_4. [e] Analytically pure sample obtained after five distillations.

lation and were characterized by ^1H, ^{13}C, and ^{31}P NMR spectroscopy and elemental analysis (Tables I and II). As expected, the alkyl-substituted phosphines are much more thermally stable than the P–Cl precursor[3] as evidenced by the fact that they could be distilled without decomposition.

Another phosphine with an even bulkier alkyl substituent was obtained by a slightly different procedure (eq 4). In this

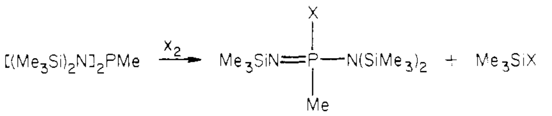


$$[(Me_3Si)_2N]_2PCl \xrightarrow[TMEDA]{Me_3SiCH(Li)Ph} [(Me_3Si)_2N]_2P—\overset{H}{\underset{Ph}{C}}—SiMe_3 \quad (4)$$

5

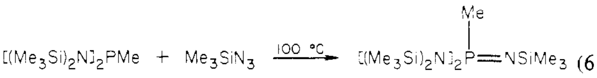
case the chloro-substituted compound was treated with the lithium derivative of Me_3SiCH_2Ph in the presence of TMEDA rather than with a Grignard reagent. Purification of the crystalline solid product was accomplished by recrystallization from pentane, and NMR spectroscopic data were used to characterize **5** (Tables I and II). Interestingly, we observed five Me_3Si signals in the room-temperature ^1H and ^{13}C NMR spectra of **5**, indicating a substantial degree of hindered P–N bond rotation.

Reactivity of $[(Me_3Si)_2N]_2PMe$. For comparison of the reactivity of bis(disilylamino)phosphines with mono(disilylamino)phosphines, some derivative chemistry of compound **1** was studied. Both similarities and differences were observed. Bromine and iodine, for example, reacted in the same manner as with the mono(disilylamino)phosphine $(Me_3Si)_2NPMe_2$,[9] forming *P*-halophosphoranimines and Me_3SiBr or Me_3SiI (eq 5). The details of these reactions are described elsewhere.[10]



$$[(Me_3Si)_2N]_2PMe \xrightarrow{X_2} Me_3SiN{=}\overset{X}{\underset{Me}{P}}—N(SiMe_3)_2 + Me_3SiX \quad (5)$$

The reaction of **1** with trimethylsilyl azide (eq 6) produced



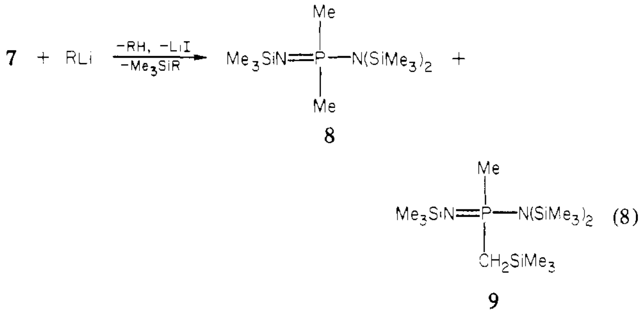
$$\underset{\mathbf{1}}{[(Me_3Si)_2N]_2PMe} + Me_3SiN_3 \xrightarrow{100\ °C} \underset{\mathbf{6}}{[(Me_3Si)_2N]_2\overset{Me}{P}{=}NSiMe_3} \quad (6)$$

the expected *N*-silylphosphoranimine (**6**). The broad singlet in the Me_3Si region of the room-temperature ^1H NMR spectrum of **6** indicates that rapid exchange of the imino and amino silyl groups occurs. At low temperatures, however, the spectrum consisted of two sharp singlets of 4:1 intensity ratio ($\Delta\nu$ = 31.2 Hz at −87 °C), which coalesced at −25 °C. The exchange barrier is, therefore, estimated to be 12.3 kcal/mol.[11] This is slightly lower than the exchange barrier of 13.5 kcal/mol[10] obtained for $(Me_3Si)_2NP(Me)_2{=}NSiMe_3$,[12] the azide product of the mono(disilylamino)phosphine $(Me_3Si)_2NPMe_2$.

Methyl iodide also reacted with **1** in the usual manner to produce the phosphonium salt **7** (eq 7), which was identified

$$\underset{\mathbf{1}}{[(Me_3Si)_2N]_2PMe} + MeI \rightarrow \underset{\mathbf{7}}{[(Me_3Si)_2N]_2PMe_2^+I^-} \quad (7)$$

by NMR spectroscopic analysis. The reaction of the phosphonium salt with *n*-BuLi or MeLi, however, was less straightforward (eq 8). The major product, compound **8**,[12]



$$\mathbf{7} + RLi \xrightarrow[-Me_3SiR]{-RH,\ -LiI} \underset{\mathbf{8}}{Me_3SiN{=}\overset{Me}{\underset{Me}{P}}—N(SiMe_3)_2} + \underset{\mathbf{9}}{Me_3SiN{=}\overset{Me}{\underset{CH_2SiMe_3}{P}}—N(SiMe_3)_2} \quad (8)$$

R = Me, *n*-Bu

results from the elimination of Me_3SiR. The expected dehydrohalogenation product, **9**, was isolated in lower yield. Compound **9** presumably forms from a [1,3] shift of a Me_3Si group from nitrogen to carbon. Similar reactions involving ylide intermediates are known to occur in systems containing only one $(Me_3Si)_2N$ group.[13]

Attempts to oxidize **1** with *t*-$BuOOSiMe_3$ to form either a silylaminophosphine oxide or a rearranged *P*-siloxyphosphoranimine were unsuccessful. After the mixture was stirred for 15 days at room temperature in CH_2Cl_2, no appreciable sign of reaction was observed. This is not unexpected in view of the steric bulk of the phosphorus substituents. In earlier work is was found that bulkier substituents markedly decrease the rate of reaction with the peroxide.[14] Other potential oxidizing agents were not investigated.

Reactions with Carbon Tetrachloride. The reactions of the bis(disilylamino)phosphines **1–5** with CCl_4 were studied in order to compare the products with those from phosphines with only one or no $(Me_3Si)_2N$ substituents. Unlike the phosphine/CCl_4 systems studied earlier[7] where only $CHCl_3$ elimination was observed (eq 1), the possibility of $CHCl_3$ and/or Me_3SiCCl_3 elimination exists with phosphines containing a $(Me_3Si)_2N$ substituent on phosphorus. In fact, both were eliminated in the reactions of compounds **1–4** with CCl_4, resulting in two new phosphorus products in each case (eq 9).

When the reactions were done without a solvent, $CHCl_3$ elimination was predominant with isolated yields of **10** ranging from 40 to 88%. Lesser amounts of **11** were observed in each reaction. The $CHCl_3$ elimination pathway corresponds to that reported earlier for phosphines without the $(Me_3Si)_2N$ group[7] where ylide products were isolated. In this case, however, the analogous ylides are presumably intermediates that readily

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(9) Wisian-Neilson, P.; Neilson, R. H. *Inorg. Chem.* **1980**, *19*, 1875.

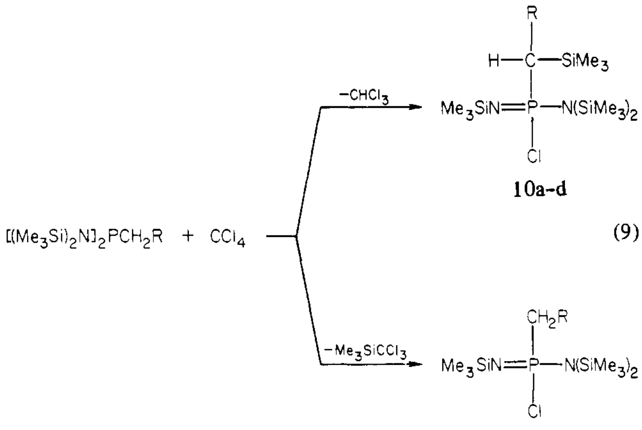
(10) Neilson, R. H.; Engenito; J. S., Jr. *Organometallics* **1982**, *1*, 1270.

(11) The equation $\Delta G_c^‡ = T_c[45.67 + 4.58 \log (T_c/\Delta\nu)]$ gives $\Delta G_c^‡$ in cal/mol with T_c in K. See: Neilson, R. H.; Wells, R. L. *Inorg. Chem.* **1977**, *16*, 7.

(12) Wilburn, J. C.; Neilson, R. H. *Inorg. Chem.* **1977**, *16*, 2519.

(13) Wilburn, J. C.; Neilson, R. H. *Inorg. Chem.* **1979**, *18*, 347.

(14) (a) Neilson, R. H.; Wisian-Neilson, P.; Wilburn, J. C. *Inorg. Chem.* **1980**, *19*, 413. (b) Wisian-Neilson, P.; Neilson, R. H., unpublished results.



$$[(Me_3Si)_2N]_2PCH_2R + CCl_4 \xrightarrow{-CHCl_3} Me_3SiN{=}\overset{\overset{\displaystyle R}{|}}{\underset{}{\overset{}{}}}\!\!\overset{H-\overset{\displaystyle |}{C}-SiMe_3}{\underset{\underset{\displaystyle Cl}{|}}{\overset{|}{P}}}-N(SiMe_3)_2 \qquad (9)$$

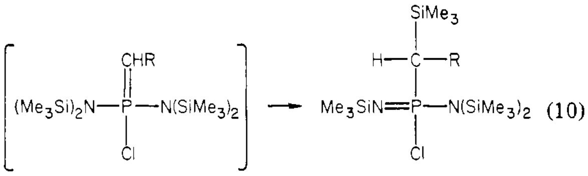
$$[(Me_3Si)_2N]_2PCH_2R + CCl_4 \xrightarrow{-Me_3SiCCl_3} Me_3SiN{=}\overset{\overset{\displaystyle CH_2R}{|}}{\underset{\underset{\displaystyle Cl}{|}}{P}}-N(SiMe_3)_2$$

10a-d

11a-d

a, R = H
b, R = Me
c, R = SiMe₃
d, R = Ph

undergo a [1,3] silyl shift from nitrogen to carbon to form compounds **10a–d** (eq 10). A similar silyl-group migration



$$\left[(Me_3Si)_2N-\overset{\overset{\displaystyle CHR}{\|}}{\underset{\underset{\displaystyle Cl}{|}}{P}}-N(SiMe_3)_2\right] \rightarrow Me_3SiN{=}\overset{\overset{\displaystyle H-\overset{\overset{\displaystyle SiMe_3}{|}}{C}-R}{|}}{\underset{\underset{\displaystyle Cl}{|}}{P}}-N(SiMe_3)_2 \qquad (10)$$

10a-d

accounts for the formation of **9** (eq 8) as well as a number of related compounds.[13]

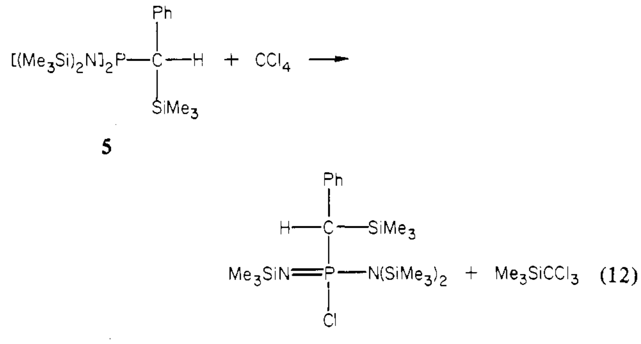
If the CCl_4 reactions of **1–4** were carried out with CH_2Cl_2 as a solvent, Me_3SiCCl_3 elimination was favored and compounds **11a–d** were isolated in 70–90% yields. Only small amounts of **10a–d** were detected in these cases. It should be noted that, although numbered differently for tabulation purposes, compounds **10a** and **11c** are identical. This compound has also been prepared by the reaction of $(Me_3Si)_2NP(CH_2SiMe_3)N_3$ and Me_3SiCl.[15] In both the solution and neat reactions, separation and purification were accomplished by careful vacuum distillation and/or sublimation of the viscous liquid and solid products. Difficulties in these separations often resulted in the isolation of reduced yields of the pure products.

The differences in the predominant products of the neat vs. CH_2Cl_2 solution reactions appears to be dependent on solvent polarity. This is supported by the fact that the reaction of **1** with CCl_4 in a nonpolar solvent such as pentane also gave **10a**, as the major product, although a somewhat lower yield was obtained than in the neat reaction. Solvent polarity should affect the nature of an ion pair of the type postulated by Appel,[6] which results from the interaction of a tertiary phosphine with CCl_4 (eq 11). The ion pair should be "tighter"

$$R_3P + CCl_4 \rightarrow R_3P\cdots Cl\cdots CCl_3 \rightarrow [R_3PCl^+][CCl_3^-] \qquad (11)$$

in a nonpolar solvent relative to that in a polar solvent. In the polar situation the relatively free CCl_3^- anion should preferentially attack the peripheral Me_3Si groups, resulting in elimination of Me_3SiCCl_3. In a nonpolar solvent, where a "tighter" ion pair exists, attack at the hydrogen on the α-carbon to eliminate $CHCl_3$ is more likely due to the close proximity of the CCl_3^- anion.

In contrast to compounds **1–4** both the neat and CH_2Cl_2 solution reactions of **5** with CCl_4 gave only the Me_3SiCCl_3 elimination product **10d** (eq 12). In this case the likelihood



$$[(Me_3Si)_2N]_2P-\overset{\overset{\displaystyle Ph}{|}}{\underset{\underset{\displaystyle SiMe_3}{|}}{C}}-H + CCl_4 \rightarrow Me_3SiN{=}\overset{\overset{\displaystyle H-\overset{\overset{\displaystyle Ph}{|}}{C}-SiMe_3}{|}}{\underset{\underset{\displaystyle Cl}{|}}{P}}-N(SiMe_3)_2 + Me_3SiCCl_3 \qquad (12)$$

5

10d

of the large CCl_3^- anion abstracting the hydrogen on the α-carbon is minimal due to the bulk of the surrounding Ph and Me_3Si groups. The Me_3SiCCl_3 elimination is thus preferred since the Me_3Si groups are more open to attack.

Further studies of these new *N*-silylphosphoranimines are currently in progress in order to assess their usefulness as precursors to low-coordinate phosphorus compounds and, ultimately, to new phosphorus–nitrogen polymer systems.

Experimental Section

General Procedures. The following reagents were purchased from commercial sources and used without further purification: PCl_3, $(Me_3Si)_2NH$, Me_3SiN_3, $PhCH_2SiMe_3$, CCl_4 (spectroscopic grade), *n*-BuLi (hexane solution), Et_2O solutions of MeLi, MeMgBr, and EtMgBr, and $PhCH_2MgCl$ (THF solution). The Grignard reagent Me_3SiCH_2MgCl was prepared in Et_2O by the published procedure.[16] Pentane, THF, Et_2O, and TMEDA were distilled from CaH_2 prior to use. Distillation from P_4O_{10} and storage over molecular sieves were used to dry CH_2Cl_2. Proton NMR spectra were recorded on a Varian EM-390 spectrometer, and $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectra were recorded on a JEOL FX-60 spectrometer. Variable-temperature spectra for **6** were recorded on the EM-390 instrument equipped with a standard Varian temperature controller, which was calibrated with a methanol reference sample. The exchange barrier was estimated by the coalescence-temperature method.[11] Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, NY. Physical, spectroscopic, and analytical data are summarized in Tables I and II.

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

Preparation of the Bis[bis(trimethylsilyl)amino]alkylphosphines, 1–4. Generally, the phosphines were prepared by the Wilburn method as described elsewhere[17] with the only modification being in the reaction stoichiometry. Typically, 1 mol of $(Me_3Si)_2NH$ was treated with 1 mol of *n*-BuLi. The resulting $LiN(SiMe_3)_2$ was allowed to react with 0.5 mol of PCl_3 and subsequently with 0.5 mol of the appropriate Grignard reagent. Yields and characterization data are listed in Tables I and II.

Preparation of Bis[bis(trimethylsilyl)amino][phenyl(trimethylsilyl)methyl]phosphine (5). TMEDA (15.1 mL, 0.10 mol) and Et_2O (120 mL) were placed in a round-bottom flask equipped with a stir bar, rubber septum, and a nitrogen inlet. The solution was cooled to 0 °C, and *n*-BuLi (60.6 mL, 1.65 M) was added via syringe. The mixture was stirred at 0 °C for 30 min. Another similarly equipped flask was charged with Me_3SiCH_2Ph (16.4 g, 0.10 mol) and Et_2O (40 mL), and this solution was cooled to 0 °C. Then the TMEDA·*n*-BuLi complex solution was transferred into the second flask via flex-needles. The mixture was stirred at 0 °C for 3 h and at room temperature for 2 h to form the TMEDA complex of $[Me_3SiC(Ph)H^-]Li^+$.

As described previously, $[(Me_3Si)_2N]_2PCl$ was prepared from $(Me_3Si)_2NH$ (41.7 mL, 0.20 mol), *n*-BuLi (121.2 mL, 1.65 M), and PCl_3 (8.7 mL, 0.10 mol) in Et_2O (200 mL). This mixture was cooled

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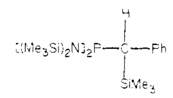
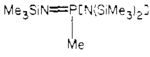
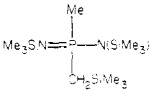
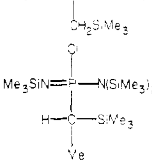
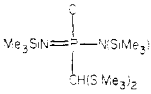
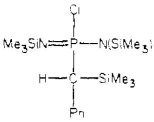
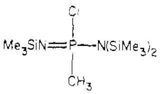
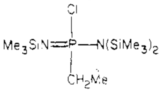
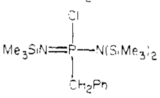
[15] Neilson, R. H. *Inorg. Chem.* **1981**, *20*, 1679.

[16] Andersen, R. A.; Wilkinson, G. *Inorg. Synth.* **1979**, *19*, 262.

[17] Neilson, R. H.; Wisian-Neilson, P. *Inorg. Chem.* **1982**, *21*, 3568.

Table II. NMR Spectroscopic Data[a]

no.	compd	signal	^{1}H NMR δ	^{1}H NMR J_{PH}	^{1}H NMR J_{HH}	^{13}C NMR δ	^{13}C NMR J_{PC}	^{31}P NMR δ
1	$[(Me_3Si)_2N]_2PCH_3$	$(Me_3Si)_2N$	0.30	1.2		5.69	6.8	105.31
		Me	1.59	11.4		25.31	34.2	
2	$[(Me_3Si)_2N]_2PCH_2Me$	$(Me_3Si)_2N$	0.31	1.2		6.25	7.3	114.36
		Me	1.08	18.6	7.2	8.55	20.1	
		CH_2	1.92[b]			29.10	28.7	
3	$[(Me_3Si)_2N]_2PCH_2SiMe_3$	$\mathit{Me}_3\mathrm{SiCH}_2$	0.15	0.9		0.29	4.9	107.12
		$(Me_3Si)_2N$	0.33	1.2		5.88	8.8	
		$\mathrm{Me_3Si}\mathit{CH}_2$	1.49	3.6		28.26	54.7	
4	$[(Me_3Si)_2N]_2PCH_2Ph$	$(Me_3Si)_2N$	0.25			5.60	7.8	112.37
		CH_2	3.31	6.9		44.69	38.1	
		Ph	7.21			132.1[b]		
5		$(Me_3Si)_2N$	−0.7[c]			5.55[d]	5.5	111.52
			0.15	2.5		6.58	4.9	
			0.33	2.7		6.74		
						7.92		
		$\mathit{Me}_3\mathrm{SiCH}$	0.37			1.05	3.2	
		$\mathrm{Me_3Si}\mathit{CH}$	3.54	6.0		42.30	64.1	
		Ph	7.02			130[b]		
6	 $Me_3SiN{=}\underset{Me}{P}[N(SiMe_3)_2]_2$	Me_3SiN	0.32[e]			5.65[e]		8.49
		Me	1.62	13.8		27.30	95.7	
9	 $Me_3SiN{=}\overset{Me}{\underset{CH_2SiMe_3}{P}}{-}N(SiMe_3)_2$	$\mathit{Me}_3\mathrm{SiCH}_2$	0.18			1.20	3.0	17.30
		Me_3SiN	0.22[e]			5.52[e]		
		$\mathrm{Me_3Si}\mathit{CH}_2$	1.25	15.0		26.67	69.0	
		Me	1.52	12.6		27.61	75.7	
10b		$\mathit{Me}_3\mathrm{SiCH}$	0.13			−0.37	2.4	27.21
		$Me_3SiN{=}$	0.23			3.78	4.9	
		$(Me_3Si)_2N$	0.44			5.64	2.4	
		Me	1.38	25.5	7.2	11.29	4.9	
		$\mathrm{Me_3Si}\mathit{CH}$	1.75[b]			33.91	98.9	
10c		$Me_3SiN{=}$	0.14			3.02	2.9	15.08
		$(\mathit{Me}_3\mathrm{Si})_2\mathrm{CH}$	0.31			3.61	4.9	
			0.36			3.93	4.9	
		$(Me_3Si)_2N$	0.47			5.69	2.9	
		$(\mathrm{Me_3Si})_2\mathit{CH}$	1.79	27.9		32.66	86.9	
10d		$\mathit{Me}_3\mathrm{SiCH}$	0.14			−0.25	3.7	11.40[f]
			0.26			0.16	2.5	14.84
		$Me_3SiN{=}$	0.19			3.66	4.9	
						3.94	3.7	
		$(Me_3Si)_2N$	0.49			5.04	2.5	
						5.60	2.5	
		$\mathrm{Me_3Si}\mathit{CH}$	3.29	21.9		50.23	102.5	
			3.31	23.1		51.41	103.8	
		Ph	7.24			128.6[b]		
11a	 $Me_3SiN{=}\overset{Cl}{\underset{CH_3}{P}}{-}N(SiMe_3)_2$	$Me_3SiN{=}$	0.12			2.50	4.9	20.30
		$(Me_3Si)_2N$	0.42			4.87		
		CH_3	2.0	15.0		30.28	107.4	
11b	 $Me_3SiN{=}\overset{Cl}{\underset{CH_2Me}{P}}{-}N(SiMe_3)_2$	$Me_3SiN{=}$	0.10			3.09	3.1	25.12
		$(Me_3Si)_2N$	0.40			5.16		
		Me	1.18	24.0	7.5	7.59	6.1	
		CH_2	2.2[b]			35.60	106.8	
11d	 $Me_3SiN{=}\overset{Cl}{\underset{CH_2Ph}{P}}{-}N(SiMe_3)_2$	$Me_3SiN{=}$	0.04			2.44	4.9	15.08
		$(Me_3Si)_2N$	0.30			4.69	2.0	
		CH_2	3.52	19.5		48.99	102.5	
			3.56	18.0				
		Ph	7.24			129.71[b]		

[a] Chemical shifts downfield from Me_4Si for ^{1}H and ^{13}C spectra and from H_3PO_4 for ^{31}P spectra; coupling constants in Hz. Solvents: ^{1}H, CH_2Cl_2; ^{13}C and ^{31}P, $CDCl_3$. [b] Multiplet. [c] Two signals were observed in benzene, indicating accidental equivalence in CH_2Cl_2. [d] Solvent for ^{13}C spectrum: C_6D_6. [e] Exchanging Me_3Si groups on nitrogen. [f] Diastereomers.

to 0 °C, and the TMEDA complex of $[Me_3SiC(Ph)H^-]Li^+$ was added via flex-needle transfer. After being stirred at 0 °C for 2 h and at room temperature for 28 h, the mixture was filtered and the solvent was removed under vacuum. Within 10 min the residue solidified. A spectroscopically pure sample of **5** was obtained by recrystallization from pentane (Tables I and II).

Preparation of *P*,*P*-Bis[bis(trimethylsilyl)amino]-*P*-methyl-*N*-(trimethylsilyl)phosphoranimine (6). Compound **1** (6.0 g, 16.3 mmol) and Me_3SiN_3 (6.2 mL, 47 mmol) were combined in a one-necked round-bottom flask equipped with a magnetic stir bar, nitrogen inlet, and reflux condenser. The solution was heated at 95–105 °C for 40 h. Vacuum distillation gave 5.3 g (72% yield) of **6**, which solidified on standing.

Formation of Bis[bis(trimethylsilyl)amino]dimethylphosphonium Iodide (7) and Reaction with Methyllithium. Compound **1** (5.91 g, 16.1 mmol) and CH_2Cl_2 (50 mL) were combined and cooled to 0 °C. Then MeI (1.1 mL, 17.6 mmol) was added via syringe. After ca. 4 h NMR spectra of the solution confirmed the formation of **7**: ^{1}H NMR (CH_2Cl_2) δ 2.18 (d, J_{PH} = 12.0 Hz, Me), 0.47 (s, Me_3Si); ^{13}C NMR ($CDCl_3$) δ 23.67 (d, J_{PC} = 76.9 Hz, Me), 4.32 (d, J_{PC} = 1.83 Hz, Me_3Si); ^{31}P NMR ($CDCl_3$) δ 57.85.

The solution of **7** was cooled to 0 °C, and MeLi (18.5 mL, 1.55 M) was added. After the mixture was stirred overnight, the solvent was removed under vacuum and the residue was distilled. Two fractions were collected. Fraction 1 (bp 55–56 °C (0.03 torr); yield 1.33 g, 27%) was identified as **8** by its ^{1}H NMR spectrum.[12] Fraction

2 (bp 72–73 °C (0.02 torr); yield 1.19 g, 21%) was identified as **9** (Tables I and II).

Reactions of Bis[bis(trimethylsilyl)amino]alkylphosphines 1–5 with CCl_4. In a typical reaction in the absence of solvent **1** (5.15 g, 14.0 mmol) was placed in a 50-mL round-bottom flask equipped with a nitrogen inlet, septum, and magnetic stir bar. After the flask was cooled to 0 °C, an excess of CCl_4 (ca. 6.5 mL) was added via syringe. After being stirred at room temperature for ca. 18 h, the mixture was distilled (Tables I and II). The major product was **10a** along with minor amounts of **11a**.

The reactions in the presence of CH_2Cl_2 were carried out in a similar fashion at 0 °C with the addition of ca. 40 mL of CH_2Cl_2 to the phosphine (ca. 14.0 mmol) before 1 molar equiv of CCl_4 was added. After the mixture was stirred at room temperature for ca. 18 h, the solvent was removed and the residue was distilled, giving **11** as the major product and smaller amounts of **10** (Tables I and II). More dilute solutions favored the formation of the Me_3SiCCl_3 elimination product **11**.

Compound **1** in pentane was also treated with CCl_4 at 0 °C. After ca. 18 h of stirring, workup and distillation afforded a 27% yield of **10a**.

Under the conditions described above, **5** reacted with either CCl_4 or CCl_4/CH_2Cl_2 to give **10d**.

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Registry No. **1**, 82581-87-1; **2**, 84050-72-6; **3**, 84050-73-7; **4**, 84050-74-8; **5**, 84050-75-9; **6**, 84050-76-0; **7**, 84050-77-1; **8**, 21385-93-3; **9**, 84056-89-3; **10a**, 76946-98-0; **10b**, 84050-78-2; **10c**, 84050-79-3; **10d**, 84050-80-6; **11a**, 84050-81-7; **11b**, 84050-82-8; **11c**, 76946-98-0; **11d**, 84050-83-9; $LiN(SiMe_3)_2$, 4039-32-1; PCl_3, 7719-12-2; $[(Me_3Si)_2N]_2PCl$, 53327-45-0; $Me_3SiCH(Li)Ph$, 37820-39-6; Me_3SiN_3, 4648-54-8; MeI, 74-88-4; MeLi, 917-54-4; *n*-BuLi, 109-72-8; CCl_4, 56-23-5; $(Me_3Si)_2NH$, 999-97-3.

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Reaction of Nitrite Ion with Hydroxylamine-*N*-sulfonate in Aqueous Solution

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The reaction between nitrite ion and hydroxylamine-*N*-sulfonate (HAMS) has been investigated in aqueous solutions; nitrous oxide and sulfate ions are the major products. The reaction kinetics exhibit first-order dependence on nitrite ion, second-order dependence on hydrogen ion in the pH region of 4–5, and between zero- and first-order dependence on HAMS, depending on the concentration. An activation energy of 30 kJ/mol was determined for the reaction in the temperature range of 10–40 °C. The ionic strength dependence was studied in the range of 0.2–1.5 M. Oxalate, tartrate, and phthalate buffer systems were found to enhance the rate of reaction to varying degrees. An empirical rate law and the determined rate constants are reported. The results are explained in terms of a mechanism that consists of the nitrosation of HAMS, followed by a decomposition into products.

Introduction

The reaction of hydroxylamine-*N*-sulfonate (also referred to as hydroxylaminesulfonate or HAMS) with nitrite ion has been known since Raschig studied the reduction of nitrous acid with sulfur dioxide.[1] Reaction between HAMS and nitrite ion was considered a side reaction in the synthesis of hydroxylamine, yielding nitrous oxide. This particular reaction, however, has become useful for the laboratory preparation of hyponitrite salts in alkaline solutions.[2,3] In acidic solutions the reaction has been much less thoroughly studied, although nitrous oxide (rather than hyponitrites) is usually formed.[4]

Our primary interest in this reaction grew out of an investigation[5] of nitrite and sulfite ion interactions in atmospheric aerosols and power-plant flue-gas scrubbers. Under sufficiently acidic conditions, nitrous oxide has been detected as a product.[6] The N_2O can result either from a direct interaction of nitrite and sulfite ions or from an indirect process involving HAMS. For a determination of the source of the gaseous product, a complete kinetic investigation of the HAMS–NO_2^- reaction was undertaken. Previously, there was only one kinetic investigation of the reaction of NO_2^- with HAMS,[4] although a number of other reactions involving HAMS and reactants in the Raschig synthesis for hydroxylamine have been investigated.[7-9]

The kinetics of the nitrite ion–HAMS reaction were investigated by Seel and Pauschmann at a HAMS concentration greater than 0.1 M.[4] The reaction rate was independent of the HAMS concentration and followed a rate law of the form

$$\text{rate} = (k[H^+] + k'[HOAC])[H^+][NO_2^-]$$

when acetate buffers were used to control the pH at a value near 5.

The nature of the buffer enhancement and the possible dependence of the reaction on HAMS at lower concentrations were not investigated.

The emphasis of this study is to evaluate the kinetics of the reaction under low-concentration conditions. By determining a rate law that may be extrapolated to concentrations of ionic species in water droplets in a polluted atmosphere, chemists

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