Lewis acid in the absence of an activation energy source.

Conclusion. Although the present study has provided us with more insight into the formation reactions of coordinatively saturated complex fluoro cations, and particularly into those involving the use of KrF^+ salts as an oxidant, there is a definite need for more experimental and theoretical work in this field to further establish the mechanisms of these interesting reactions.

Acknowledgment. We are indebted to Drs. C. J. Schack and L. R. Grant for helpful discussions, to Drs. I. B. Goldberg and T. McKinney for ESR measurements, and to the Army Research Office and the Office of Naval Research for financial support of this work.

Registry No. $KrFSbF_6$, 52708-44-8; SbF_5, 7783-70-2; NF_3, 7783-54-2; NF_4AsF_6, 16871-75-3; BF_3, 7637-07-2; NF_4BF_4, 15640-93-4; $NF_4Sb_2F_{11}$, 58702-89-9; PtF_6, 13693-05-5; NF_4PtF_6, 90025-87-9; ClF_5, 13637-63-3; F_2, 7782-41-4; ClF_4PtF_6, 38123-69-2; ClF_6PtF_6, 36609-91-3; BrF_5, 7789-30-2; AsF_5, 7784-36-3.

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Reactions of Mono(disilylamino)phosphines with Carbon Tetrachloride[1]

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A series of mono(disilylamino)phosphines $(Me_3Si)_2NPRR'$ (R, R′ = Me, Et, *i*-Pr, *t*-Bu, CH_2SiMe_3, $CH_2CH{=}CH_2$, CH_2Ph, Ph, NMe_2, OMe, OCH_2CF_3) and two related phosphines, $Me_2\overline{SiCH_2CH_2Me_2SiN}P(t\text{-}Bu)CH_2SiMe_3$ and $(t\text{-}BuMe_2Si)_2NPMe_2$, were treated either with neat CCl_4 or with CCl_4 in CH_2Cl_2. The reactions proceeded with elimination of $CHCl_3$ and/or Me_3SiCCl_3 to form a variety of new *P*-chloro-*N*-silylphosphoranimines of general formula $Me_3SiN{=}P(Cl)R'R''$. The preferential course of the reaction was dependent on solvent polarity and on the electronic and steric influence of the substituents at nitrogen and phosphorus. Complete physical and spectroscopic (^1H, ^{13}C, and ^{31}P NMR) characterization data are given for the new phosphines and *P*-chloro-*N*-silylphosphoranimines.

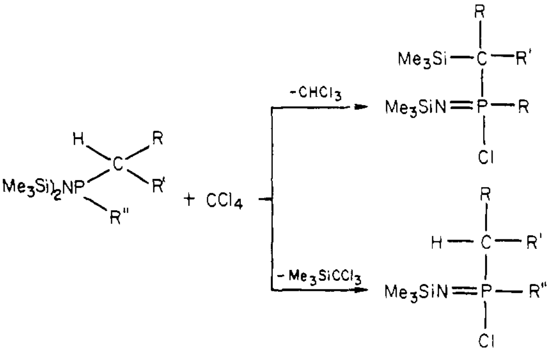
Introduction

Due to the reactivity of the silicon–nitrogen bond, the chemistry of (disilylamino)phosphines, i.e. $(Me_3Si)_2NPRR'$, often differs substantially from that of simple alkyl- or aryl-substituted phosphines.[2] As part of our continuing study of the reactivity of silicon–nitrogen–phosphorus compounds, we have investigated the oxidation reactions of a variety of bis(disilylamino)phosphines[3] and mono(disilylamino)phosphines with CCl_4.

The reaction of CCl_4 with tertiary phosphines that contain a CH proton α to phosphorus, but no disilylamino groups, produces $CHCl_3$ and phosphorus ylides.[4] This presumably occurs via initial formation of an ion-pair intermediate $[R_3PCl^+][CCl_3^-]$[5] with subsequent attack at the hydrogen by the CCl_3^- anion.

It was shown earlier that an alternate reaction pathway also becomes important when CCl_4 interacts with phosphines containing both an α-hydrogen and two disilylamino groups.[3] In addition to proton abstraction by the CCl_3^- anion, attack at a silicon–nitrogen bond may occur with elimination of Me_3SiCCl_3. The competition between these two pathways is influenced by the steric bulk of the substituents at phosphorus and by solvent polarity.

In this paper, we report the reactions of CCl_4 with mono(disilylamino)phosphines that contain α-hydrogens. As in the reactions of CCl_4 with bis(disilylamino)phosphines, both the silicon–nitrogen bond and the α-hydrogens are potentially reactive sites. Two different types of *N*-silylphosphoranimine products may, therefore, be produced from these reactions (eq 1).



(1)

Our primary objectives were (a) to compare the CCl_4 reaction products with those obtained from bis(disilylamino)phosphines or from tertiary phosphines with no disilylamino substituents, (b) to better understand the influence of steric and electronic differences of substituents at phosphorus, i.e. R, R′, and R″, and (c) to prepare various *P*-chloro-*N*-silylphosphoranimines, which are potential precursors to polyphosphazenes and to novel three-coordinate phosphorus compounds.

Results and Discussion

Phosphine Synthesis. The various bis(disilylamino)phosphines used in this study can be divided into four general categories: (1) simple dialkyl- or alkyl(phenyl)phosphines (**1** – **7**); (2) ((trimethylsilyl)methyl)phosphines (**8**–**14**); (3) phosphines with benzyl or allyl substituents (**15**–**18**); (4) systems with *N*-silyl groups other than Me_3Si (**19** and **20**).

Many of these phosphines were prepared as described previously by using the Wilburn procedure[6] or related methods.[7,8] Of the compounds reported here for the first time, phosphines **8** and **13** were prepared by the nucleophilic sub-

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[1] (a) 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; INOR 147. (b) Ford, R. R.; Goodman, M. A.; Li, B.-L.; Neilson, R. H.; Roy, A. K.; Wettermark, U. G.; Wisian-Neilson, P.; Xie, Z.-M. Proceedings of the XVII Organosilicon Symposium, Fargo, ND, June 1983.

[2] Morton, D. W.; Neilson, R. H. *Organometallics* **1982**, *1*, 289 and references sited therein.

[3] Li, B.-L.; Engenito, J. S., Jr.; Neilson, R. H.; Wisian-Neilson, P. *Inorg. Chem.* **1983**, *22*, 575.

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

[5] Appel, R. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 801.

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

[7] O'Neal, H. R.; Neilson, R. H. *Inorg. Chem.* **1983**, *22*, 814.

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

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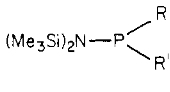
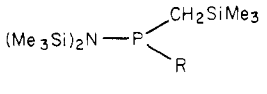
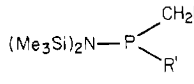


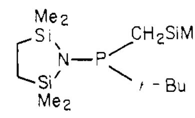


1: R = R' = Me
2: R = R' = Et
3: R = R' = *i*-Pr
4: R = *i*-Pr, R' = *t*-Bu
5: R = Ph, R' = Me
6: R = Ph, R' = Et
7: R = Ph, R' = *i*-Pr

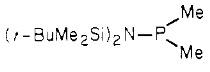
8: R = Me
9: R = CH_2SiMe_3
10: R = Ph
11: R = *t*-Bu
12: R = OMe
13: R = OCH_2CF_3
14: R = NMe_2



15: R = Ph, R' = Ph
16: R = Ph, R' = CH_2Ph
17: R = CH=CH_2, R' = Ph
18: R = CH=CH_2, R' = CH_2CH=CH_2



19



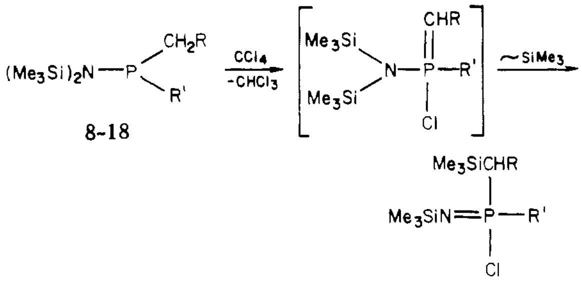
20

stitution reactions of MeMgBr or CF_3CH_2OH with $(Me_3Si)_2NP(Cl)CH_2SiMe_3$.[8] Compound **10** was made from $(Me_3Si)_2NP(Cl)Ph$[6] and Me_3SiCH_2MgCl.[9] Repeated distillations failed to give an analytically pure sample of **10**, but a satisfactory analysis was obtained for **23**, the *P*-chloro-*N*-silylphosphoranimine derivative obtained from its reaction with CCl_4. The preparation of dimethylamino compound **14**[10a] involved the sequential reaction of $Me_3SiCH_2PCl_2$ with Me_3SiNMe_2 and $LiN(SiMe_3)_2$. Allyl and benzyl Grignard reagents were used in the Wilburn synthesis[6] to prepare phosphines **15–18**. Compounds **15–17** each had broad boiling point ranges and failed to give satisfactory elemental analyses. As in the case of **10**, however, the trace impurities in these phosphines were not detectable in their NMR spectra. Moreover, good analytical data were obtained for *P*-chlorophosphoranimine derivatives **28** and **29**, the decomposition product of **30**, and several other derivatives.[11] Compounds **19** and **20** were made by procedures similar to those above by using $(t\text{-BuMe}_2Si)_2NH$[12] and $\overline{Me_2SiCH_2CH_2SiMe_2N}H$[13] in place of $(Me_3Si)_2NH$.

Preparative and ^{31}P NMR spectral data for these new compounds are listed in Table II. The ^1H and ^{13}C NMR data for selected compounds are given in Table I with complete spectral and analytical data included as supplementary material. The ^1H NMR spectra of several compounds (**8**, **10**, **13**, **15**, **16**) show that the CH_2 protons of the CH_2SiMe_3 and CH_2Ph groups are diastereotopic. The splitting pattern of these protons is a typical AB portion of an ABX spectrum (X = ^{31}P). Standard procedures for analysis of an ABX spectrum[14] were used to determine the chemical shifts and coupling constants. The ^1H NMR spectra of phosphines **17–19** could not be analyzed in detail since the patterns were significantly complicated by the signals of other CH and/or CH_2 protons.

CCl_4 Reactions. The reactions of mono(disilylamino)phosphines with carbon tetrachloride are grouped into two general categories: (a) those that result only in elimination of $CHCl_3$; (b) those that proceed with elimination of both $CHCl_3$ and Me_3SiCCl_3. These groups are discussed independently below.

(a) $CHCl_3$ Elimination. Despite the presence of the disilylamino group on phosphorus, a large number of phosphines with α-hydrogens were found to react with CCl_4 in the same manner as tertiary alkylphosphines,[4] giving only $CHCl_3$ elimination (eq 2). Unlike simple tertiary phosphines, however,



8–18

(2)

21: R = $SiMe_3$, R' = Me
22: R = $SiMe_3$, R' = CH_2SiMe_3
23: R = $SiMe_3$, R' = Ph
24: R = $SiMe_3$, R' = *t*-Bu
25: R = $SiMe_3$, R' = OMe
26: R = $SiMe_3$, R' = OCH_2CF_3
27: R = $SiMe_3$, R' = NMe_2
28: R = R' = Ph
29: R = Ph, R' = CH_2Ph
30: R = CH=CH_2, R' = Ph
31: R = CH=CH_2, R' = CH_2CH=CH_2

the products are *P*-chloro-*N*-silylphosphoranimines and not phosphorus ylides. The ylides are presumably intermediates that undergo a rapid [1,3] silyl shift from nitrogen to carbon to form *N*-silylphosphoranimines **21–31**. There is precedence for such a silyl shift in a number of related systems.[3,15] Several features of the ^1H and ^{13}C NMR spectra of the products indicated that the phosphoranimines, rather than the ylides, were indeed obtained. In fact, none of these compounds exhibited the upfield chemical shifts typical of ylides in either the ^1H or ^{13}C NMR spectra (^1H, ca. δ -0.8; ^{13}C, δ ca. -7.0).[16] The presence of a $(Me_3Si)_2CH$ group in compounds **21–27** is indicated by the observation of three Me_3Si signals in the ^1H NMR. One signal is the imino group, Me_3SiN=, and the others are the C-bonded diastereotopic Me_3Si groups adjacent to a chiral phosphorus. Evidence for the nonequivalence of the two Me_3Si groups on carbon is provided by the chemical shift changes of these signals, which occur upon changing the solvent from benzene to CH_2Cl_2.

The observation of two distinct Me_3Si signals in the ^1H and ^{13}C NMR spectra as well as the lack of typical ylide signals is consistent with the phosphoranimine structures for **28** and **29**. In addition, the P–C–H signals in the ^1H and ^{13}C NMR spectra of **30** and **31** had large J_{PH} (13–18 Hz) and J_{PC} (80–83 Hz) couplings as well as ^1H NMR chemical shifts indicative of allylic (2–3 ppm) rather than vinylic (5–6 ppm) protons.[17] Two signals were observed in the ^{31}P NMR spectra of **28–31** due to the diastereomers that result from the presence of two chiral centers in these molecules.

With the exception of compound **30**, derived from allylphenylphosphine **17**, these new phosphoranimines were isolated and purified by vacuum distillation. They were identified by NMR spectroscopy and also characterized by elemental analysis. Compound **30** was a high-boiling material that was best purified by recrystallization, after which NMR spectra indicated that very little impurity remained. Attempted

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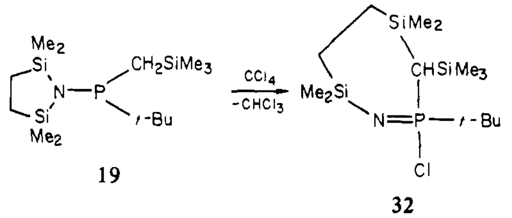
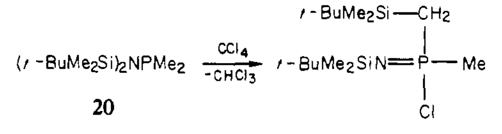
(9) Andersen, R. A.; Wilkinson, G. *Inorg. Synth.* **1979**, *19*, 262.
(10) (a) Thoma, R. J. Ph.D. Dissertation, Texas Christian University, Fort Worth, TX, 1984. (b) Ford, R. R. Ph.D. Dissertation, Texas Christian University, Fort Worth, TX, 1984.
(11) Roy, A. K. Ph.D. Dissertation, Texas Christian University, Fort Worth, TX, 1984.
(12) West, R.; Boudjouk, P. *J. Am. Chem. Soc.* **1973**, *95*, 3983.
(13) Baney, R. H., Haberland, G. G. *J. Organomet. Chem.* **1966**, *5*, 320.
(14) Becker, E. D. "High Resolution NMR"; Academic Press: New York, 1969; p 152.
(15) Wilburn, J. C.; Neilson, R. H. *Inorg. Chem.* **1979**, 18, *347*.
(16) Schmidbaur, H.; Buchner, W.; Scheutzow, D. *Chem. Ber.* **1973**, *106*, 1251.
(17) Morton, D. W.; Neilson, R. H. *Organometallics* **1982**, *1*, 623.

distillation of the purified material resulted in decomposition via elimination of Me_3SiCl. The residue after heating was identified as $\{[CH_2{=}CHC(SiMe_3)H]P(Ph){=}N\}_n$ by elemental analysis and ^{31}P NMR (see Experimental Section).

Two related phosphines, **19** and **20**, with different silyl substituents at nitrogen also reacted with CCl_4 to produce only $CHCl_3$ elimination products (eq 3 and 4). The seven-membered ring compound **32** is analogous to that obtained from a similar [1,3] silyl shift upon treatment of $\overline{\text{Me}_2\text{SiCH}_2\text{CH}_2\text{Me}_2\text{SiN}}\text{PMe}_3{}^+\text{I}^-$ with *n*-BuLi.[15] As noted in this earlier case, the formation of the cyclic compound strongly suggests that the silyl shift from nitrogen to carbon is an intramolecular process. The reaction of **20** with CCl_4 (eq 4) is also consistent with the process being intramolecular. In contrast to $(Me_3Si)_2NPMe_2$ (**1**), which is discussed later, **20** gives exclusively the $CHCl_3$ elimination product **33** either with CH_2Cl_2 as a solvent or in excess CCl_4. Presumably the conformation of the bulk *tert*-butyl group prevents the external attack of the CCl_3^- anion at silicon [which readily occurs with less hindered groups in $(Me_3Si)_2NPMe_2$] but does not interfere with an internal attack at silicon by an ylidic carbon within the same molecule.

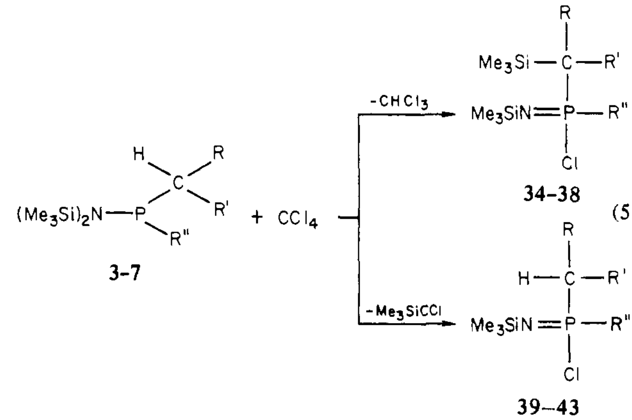

19 32 (3)


$$(t\text{-BuMe}_2\text{Si})_2\text{NPMe}_2 \xrightarrow[-\text{CHCl}_3]{\text{CCl}_4} t\text{-BuMe}_2\text{SiN}{=}\underset{\text{Cl}}{\overset{t\text{-BuMe}_2\text{Si}-\text{CH}_2}{\text{P}}}-\text{Me} \qquad (4)$$

20 33

A common feature in most of the phosphines involved in these reactions is the acidic character of the α protons. Attack of the CCl_3^- anion on these protons is likely because the resulting ylide intermediates are resonance stabilized by the adjacent $SiMe_3$, $CH{=}CH_2$, or Ph groups. Once formed, the ylides may then easily rearrange via a [1,3] silyl shift. We have noted only a few exceptions to this generalization. As reported previously,[3] $[(Me_3Si)_2N]_2PCH_2R$ (R = $SiMe_3$, Ph) reacted with CCl_4 to give both $CHCl_3$ and Me_3SiCCl_3 elimination products. Formation of Me_3SiCCl_3 in these cases is not surprising since there are a large number of Me_3Si groups available for attack by the CCl_3^- anion. Another exception occurred in this series. The reaction of $(Me_3Si)_2NP(CH_2SiMe_3)Me$ (**8**) in CH_2Cl_2 produced only the $CHCl_3$ elimination product **21**, but in excess CCl_4 with no other solvent another phosphorus compound was also formed as indicated by ^{31}P NMR (δ 25.5). Although it was not possible to separate this second product from **21**, NMR analysis indicated that the CCl_3^- anion may also have attacked the hydrogens on the PMe group.

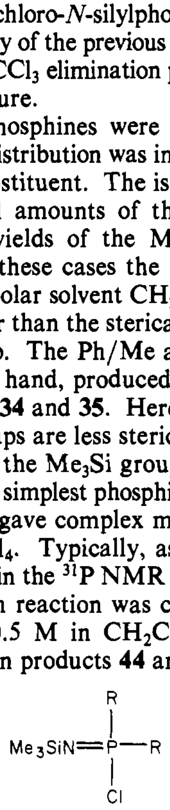
(b) $CHCl_3$ and Me_3SiCCl_3 Elimination. The reactions of mono(disilylamino)phosphines containing simple alkyl groups (i.e. Me, Et, *i*-Pr) with CCl_4 were often more complicated. Generally, both $CHCl_3$ and Me_3SiCCl_3 elimination products were formed (eq 5), with a change in solvent having a profound effect on which products were predominant. This is in contrast to most of the reactions described above where only $CHCl_3$ elimination was observed either in CH_2Cl_2 or in excess CCl_4. Table III summarizes the yields of each type of product obtained when these reactions were done in CH_2Cl_2 and in excess CCl_4.


3-7 34-38 39-43 (5)

When these reactions were carried out neat (i.e. excess CCl_4), the favored products were always those resulting from the elimination of $CHCl_3$ (**34**–**38**). For reasons similar to those discussed above, these products were identified by NMR spectroscopy as the *P*-chloro-*N*-silylphosphoranimines and not the ylides. Unlike many of the previous reactions, at least trace amounts of the Me_3SiCCl_3 elimination products were observed in each reaction mixture.

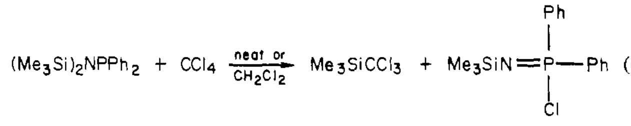
When the same phosphines were treated with CCl_4 in CH_2Cl_2, the product distribution was influenced by the nature of the phosphorus substituent. The isopropylphosphines (**3**, **4**, **7**) produced small amounts of the $CHCl_3$ elimination products and large yields of the Me_3SiCCl_3 elimination products, **41**–**43**. In these cases the CCl_3^- anion, which is relatively free in the polar solvent CH_2Cl_2, preferentially attacks the silicon rather than the sterically hindered hydrogen in the isopropyl group. The Ph/Me and Ph/Et phosphines **5** and **6**, on the other hand, produced primarily the $CHCl_3$ elimination products, **34** and **35**. Here the hydrogens of the methyl and ethyl groups are less sterically crowded so there is less competition by the Me_3Si group for the CCl_3^- anion.

The reactions of the simplest phosphines $(Me_3Si)_2NPR_2$ (**1**, R = Me; **2**, R = Et) gave complex mixtures of products in either CH_2Cl_2 or CCl_4. Typically, as many as four major signals were observed in the ^{31}P NMR spectra of the reaction mixtures. When each reaction was carried out under very dilute conditions (<0.5 M in CH_2Cl_2), low yields of the Me_3SiCCl_3 elimination products **44** and **45** were isolated by distillation. No other pure compounds could be isolated from any of the reaction mixtures. In view of the clean reaction (eq 4) observed for the analogous $(t\text{-BuMe}_2\text{Si})_2\text{N}$-substituted phosphine **20**, these results show that the nature of the silicon substituents can also significantly influence the course of such reactions.


$$\text{Me}_3\text{SiN}{=}\underset{\text{Cl}}{\overset{\text{R}}{\text{P}}}-\text{R}$$

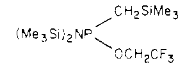
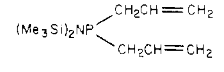
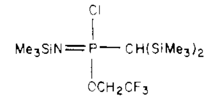
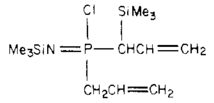
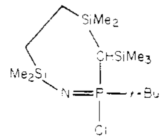
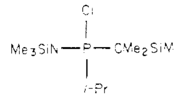
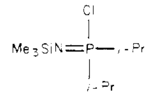
44: R = Me
45: R = Et

One reaction of CCl_4 with a mono(disilylamino)phosphine with no α-hydrogens was also investigated (eq 6). As expected, the Me_3SiCCl_3 elimination product **46** was obtained. On heating in a sealed glass ampule, **46** eliminated Me_3SiCl, forming $(Ph_2PN)_3$. This is analogous to the thermal decomposition of $Me_3SiN{=}P(X)Ph_2$ (X = F,[18] Br[19]).


$$(\text{Me}_3\text{Si})_2\text{NPPh}_2 + \text{CCl}_4 \xrightarrow[\text{CH}_2\text{Cl}_2]{\text{neat or}} \text{Me}_3\text{SiCCl}_3 + \text{Me}_3\text{SiN}{=}\underset{\text{Cl}}{\overset{\text{Ph}}{\text{P}}}-\text{Ph} \qquad (6)$$

46

Table I. ^{1}H and ^{13}C NMR Spectroscopic Data for Selected Compounds[a]

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}
 13	$(Me_3Si)_2N$	0.32	1.5		4.55	8.6
	Me_3SiCH_2	0.15	0.9		0	4.9
	$Me_3Si\mathit{CH}_2$	0.88	7.3	13.8	27.41	39.1
		1.75	1.8	13.8		
	$O\mathit{CH}_2CF_3$	3.93	7.2[c]		65.50	23.2[c]
	$OCH_2\mathit{CF}_3$				124.38	13.4[d]
 18	$(Me_3Si)_2N$	0.37[e]	1.2		4.79	7.3
	$\text{-}\mathit{CH}_2CH{=}CH_2$	2.27-2.91[b,e]			38.03	23.8
	$\text{-}CH_2\mathit{CH}{=}CH_2$	5.63-6.17[b,e]			134.23	12.8
	$\text{-}CH_2CH{=}\mathit{CH}_2$	4.94-5.27[b,e]			116.44	10.4
 26	Me_3SiN	0.08			2.90	5.5
	$(\mathit{Me}_3Si)_2CH$	0.24			1.81	4.3
		0.31				
	$(Me_3Si)_2\mathit{CH}$	1.31	27.0		27.71	100.7
	$O\mathit{CH}_2CF_3$	4.20	8.4[f]		60.69	7.3[g]
	$OCH_2\mathit{CF}_3$				123.48	14.7[h]
 31	Me_3SiN	−0.02	0.6		3.29	4.9
	Me_3SiCH	0.21			0.69	2.4
		0.22			0.85	2.4
	$Me_3Si\mathit{CH}$	2.3-3.0[b]			45.87	80.0
					43.17	80.6
	$SiCH\mathit{CH}{=}CH_2$	4.7-5.4[b,e]			132.22	7.3
					131.82	8.5
	$SiCHCH{=}\mathit{CH}_2$	5.5-6.1[b,e]			120.81	14.7
					120.63	14.0
	$P\mathit{CH}_2CH{=}CH_2$	2.3-3.0[b]			44.37	70.2
					44.13	70.2
	$PCH_2\mathit{CH}{=}CH_2$	4.7-5.4[b,e]			128.93	10.4
					128.53	9.8
	$PCH_2CH{=}\mathit{CH}_2$	5.5-6.1[b,e]			117.80	17.1
					118.21	15.9
 32	MeSi	0.01-0.38[b]			1.17-5.52[b]	
	$Me_3Si\mathit{CH}$	1.56	13.8		25.24	32.2
	$SiCH_2$	0.64-0.97[b]			11.50	
					12.93	
	Me_3C	1.19	19.2		25.40	
	$Me_3\mathit{C}$				40.45	88.9
 37	Me_3SiN	0.18			3.43	4.3
	Me_3SiC	0.03			−1.46	
	$Me_3Si\mathit{C}$				32.04	65.9
	Me_2C	1.08-1.41[b]			20.99	4.9
					20.79	1.3
	Me_2CH	1.08-1.41[b]			19.51	3.1
					18.76	3.7
	$Me_2\mathit{CH}$	2.05-2.41[b]			34.90	71.4
 42	Me_3SiN	0.02			3.37	4.9
	Me_2CH	1.20	19.2	6.8	16.43	3.1
					16.00	3.7
	$Me_2\mathit{CH}$	2.19	6.9	6.9	32.45	78.1

[a] Chemical shifts downfield from Me_4Si for ^{1}H and ^{13}C spectra, coupling constants in Hz. Solvents (unless noted otherwise): ^{1}H, CH_2Cl_2; ^{13}C, $CDCl_3$. [b] Multiplet. [c] $J_{HF} = 9.0$ Hz; $J_{FC} = 35.4$ Hz. [d] $J_{FC} = 278.3$ Hz. [e] Solvent: benzene. [f] Couplings in benzene; $J_{FH} = 8.4$ Hz. [g] $J_{FC} = 37.2$ Hz. [h] $J_{FC} = 277.7$ Hz.

Conclusion. Several trends become evident from the results of this series of reactions as well as those involving bis(disilylamino)phosphines. The elimination of both $CHCl_3$ and Me_3SiCCl_3 are reasonable pathways for these reactions to follow. The elimination of $CHCl_3$ is favored by (a) nonpolar solvents that promote a "tighter" intermediate ion pair $[R_3PCl^+][CCl_3^-]$, resulting in preferential attack of the CCl_3^- anion on the nearby α-hydrogen; (b) substituents at the α-carbon (e.g. $SiMe_3$, Ph, $CH{=}CH_2$) that tend to resonance stabilize the ylide intermediate; and (c) α-hydrogens that are not sterically hindered by other substituents on the α-carbon. The elimination of Me_3SiCCl_3 is favored by (a) polar solvents that allow for a relatively "loose" ion pair and a CCl_3^- anion that is free to attack a peripheral Me_3Si group; (b) an abundance of $(Me_3Si)_2N$ groups[3] so there is a greater chance for attack at silicon; and (c) sterically hindered α-hydrogens that limit their accessibility by the CCl_3^- anion.

Experimental Section

General Procedures. The following reagents were purchased from commercial sources and used without further purification: $MeMgBr(Et_2O)$, $PhCH_2MgCl(THF)$, *t*-BuLi(pentane), $CH_2{=}CHCH_2MgCl(Et_2O)$, CF_3CH_2OH, $PhPCl_2$. Spectroscopic grade CCl_4 was stored over molecular sieves. Dichloromethane, Et_2O, and Et_3N were distilled from CaH_2 prior to use. Published procedures were used to prepare $Me_2\overline{SiCH_2CH_2Me_2SiN}H$,[13] Me_3SiCH_2MgCl,[9]

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(18) Wisian-Neilson, P.; Neilson, R. H.; Cowley, A. H. *Inorg. Chem.* **1977**, *16*, 1460.

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

Table II. Preparative and ^{31}P NMR Spectroscopic Data

compd	preparative % yield[a]	 bp, °C (*P*, mm)	^{31}P NMR δ[b]
8	66	37-38 (0.01)	36.29
10	61	98-100 (0.01)	41.95
13	73	40-42 (0.01)	165.49
15	78	115-150 (0.05)	54.36
16	62	133-143 (0.10)	62.53
17	65	73-90 (0.02)	46.96
18	65	71-73 (0.03)	49.61
19	56	65-69 (0.01)	56.66
20	75	70-76 (0.05)	31.21
21	76	51 (0.01)	26.97
22	(71)	69-75 (0.01)[f]	29.06
23	(61)	82-86 (0.01)	19.66
24	84	75-80 (0.03)	49.71
25	(82)	48 (0.01)	15.16
26	(78)	66-68 (0.01)	12.13
27	(75)	61-62 (0.01)	21.80
28	84	124-126 (0.05)	18.58, 16.93[c]
29	(87)	130-137 (0.05)	22.62, 24.03[c]
30	75[d]	104 (0.05)[e]	17.72, 16.48[c]
31	(84)	70-78 (0.15)	25.53, 23.40[c]
32	(62)	80-80.5 (0.01)	52.14, 44.17[c]
33	(72)	80-82 (0.03)	23.53
34	(80)	77-81 (0.10)	16.63
35	(82)	118 (0.10)	25.80, 27.04[c]
36	(33)	92 (0.03)	35.94
37	(75)	62 (0.07)	54.01
38	(52)	70-72 (0.07)	57.42
40	8	87-96 (1.3)	24.03
41	82	68-70 (0.01)	30.63
42	77	38 (0.15)	50.77
43	95	38-40 (0.05)	54.55
44	28	46-47 (4.7)	23.05
45	42	60-61 (1.2)	39.07
46	(74)	110 (0.05)	11.30

[a] Values in parentheses are yields from neat $\mathrm{CCl_4}$ reactions. Other yields for **21**-**46** are from $\mathrm{CCl_4}$ reactions in $\mathrm{CH_2Cl_2}$. [b] Chemical shifts downfield from $\mathrm{H_3PO_4}$. Solvent: $\mathrm{CDCl_3}$. [c] Diastereomers. [d] Estimated yield from recrystallization. [e] Only a few drops distilled before decomposition. [f] mp 38-41 °C.

$\mathrm{(Me_3Si)_2NLi}$,[6] and $(t\text{-}\mathrm{BuMe_2Si)_2NH}$.[12] The mono(disilylamino)phosphines **1**-**7**, **9**, **11**, and **12** were also prepared by published procedures.[6-8] Proton NMR spectra were recorded on a Varian EM390 spectrometer, while a JEOL FX-60 spectrometer was used to record $^{13}\mathrm{C}\{^1\mathrm{H}\}$ and $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR spectra. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, NY. Table I contains ^{1}H and ^{13}C NMR data for representative compounds. Physical, preparative, and ^{31}P NMR data for all the compounds reported here are listed in Table II.

All reactions and manipulations were carried out under an atmosphere of dry nitrogen or under vacuum. Typical procedures used in the preparation of the new compounds in this report are described below.

Preparation of $\mathrm{(Me_3Si)_2NP(Me)CH_2SiMe_3}$ (8). The chlorophosphine $\mathrm{(Me_3Si)_2NP(Cl)CH_2SiMe_3}$[8] (31.08 g, 99 mmol) and $\mathrm{Et_2O}$ (100 mL) were placed in a three-necked, round-bottom flask equipped with a magnetic stir bar, a nitrogen inlet, and an addition funnel. The reaction flask was cooled to 0 °C and MeMgBr (36.7 mL, 2.7 M, 99 mmol) was added dropwise via the addition funnel. The mixture was allowed to warm to room temperature and to stir overnight. The Grignard salts were removed from the mixture by filtration under nitrogen, and solvent was removed from the filtrate under reduced pressure. Distillation of the yellow liquid residue through a 10-cm Vigreux column yielded 19.0 g of a colorless liquid that was identified as **8**.

Preparation of $\mathrm{(Me_3Si)_2NP(OCH_2CF_3)CH_2SiMe_3}$ (13). A three-necked round-bottom flask equipped with a magnetic stir bar, a nitrogen inlet, and a septum was charged with $\mathrm{(Me_3Si)_2NP(Cl)CH_2SiMe_3}$[8] (18.4 g, 58.6 mmol), $\mathrm{Et_3N}$ (8.2 mL, 58.8 mmol), and $\mathrm{Et_2O}$ (50 mL). The mixture was cooled to 0 °C and $\mathrm{CF_3CH_2OH}$ (4.6 mL, 58.6 mmol) was added slowly via syringe. This mixture was warmed to room temperature and stirred for ca. 2 h. Filtration under nitrogen removed $\mathrm{Et_3N{\cdot}HCl}$. Solvent was removed from the filtrate affording a colorless residue that was distilled under vacuum through a 10-cm Vigreux column to give 16.1 g of **13** as a colorless liquid.

Preparation of $\mathrm{(Me_3Si)_2NP(Ph)CH_2SiMe_3}$ (10). A three-necked, round-bottom flask equipped with a mechanical stirrer, a nitrogen inlet, and an addition funnel was charged with $\mathrm{PhPCl_2}$ (27.2 mL, 0.20 mol) and $\mathrm{Et_2O}$ (100 mL), and the mixture was cooled to -78 °C. A solution of $\mathrm{(Me_3Si)_2NLi}$ (0.20 mol in ca. 200 mL of hexane[6]) was added dropwise via the addition funnel. The mixture was then warmed to 0 °C, stirred at that temperature for 2 h, and then warmed to room temperature and stirred overnight. This mixture was cooled to 0 °C, and $\mathrm{Me_3SiCH_2MgCl}$[9] (0.20 mol in ca. 200 mL of $\mathrm{Et_2O}$) was added dropwise. After warming to room temperature and stirring for ca. 5 h, the mixture was filtered under nitrogen. Solvent removal at reduced pressure gave a yellow residue that was distilled through a 10-cm Vigreux column to give 43.3 g of a colorless liquid that solidified on standing (mp 30-31 °C) and was identified as **10**.

Preparation of $\mathrm{Me_2\overline{SiCH_2CH_2Me_2SiN}P(\mathit{t}\text{-}Bu)CH_2SiMe_3}$ (19). A procedure similar to that used to prepare $\mathrm{(Me_3Si)_2NP(Cl)CH_2SiMe_3}$[8] was used to prepare $\mathrm{Me_2\overline{SiCH_2CH_2Me_2SiN}P(Cl)CH_2SiMe_3}$.[10b] This chlorophosphine (19.8 g, 63.5 mmol) and $\mathrm{Et_2O}$ (50 mL) were placed in a three-necked, round-bottom flask equipped with a nitrogen inlet, a magnetic stir bar, and a septum. After the solution was cooled to 0 °C, *t*-BuLi (32.0 mL, 2 M) was added via syringe. The mixture was warmed to room temperature and stirred overnight. Filtration, solvent removal from the filtrate, and distillation of the residue gave **19**.

Synthesis of 15-18 and 20 by the Wilburn Method. Typically 250-350 mmol of **15**-**18** was prepared according to the Wilburn[6] procedure using $\mathrm{PhCH_2MgCl}$ or $\mathrm{CH_2{=}CHCH_2MgCl}$. Compound **20** was also prepared by the Wilburn procedure using $(t\text{-}\mathrm{BuMe_2Si)_2NH}$ in place of $\mathrm{(Me_3Si)_2NH}$.

Reactions of (Disilylamino)phosphines with $\mathrm{CCl_4}$. Unless otherwise noted, the following procedures are typical of those used to prepare *P*-chloro-*N*-silylphosphoranimines **21**-**46**.

(a) Neat Reactions. (Disilylamino)phosphine **3** (6.60 g, 23.8 mmol) was placed in a 100-mL round-bottom flask equipped with a magnetic stir bar, nitrogen inlet, and septum. After it was cooled to 0 °C, a fivefold excess (11.5 mL, 118.9 mmol) of $\mathrm{CCl_4}$ was added to the phosphine via syringe. The mixture was stirred overnight at room temperature, and a yellow solution formed. Excess $\mathrm{CCl_4}$ and other volatiles were removed under reduced pressure. Vacuum distillation of the residue afforded **37**.

(b) Reactions in $\mathrm{CH_2Cl_2}$. In a similar setup, phosphine **3** (4.86 g, 17.5 mmol) and $\mathrm{CH_2Cl_2}$ (18 mL) were placed in the flask and cooled to 0 °C. One molar equivalent (1.7 mL, 17.5 mmol) of $\mathrm{CCl_4}$ was then added via syringe. Solvent removal at reduced pressure and distillation of the yellow liquid residue gave **42**.

Table III. Percent Yields of Products Obtained via Eq 5[a]

R	R′	R″	$\mathrm{CHCl_3}$ elimination compd	 neat	 $\mathrm{CH_2Cl_2}$	$\mathrm{Me_3SiCCl_3}$ elimination compd	 neat	 $\mathrm{CH_2Cl_2}$
H	H	Ph	**34**	80	79	**39**	t	t
Me	H	Ph	**35**	82	25	**40**	t	8
Me	Me	Ph	**36**	33	t	**41**	12	82
Me	Me	*i*-Pr	**37**	75	t	**42**	t	77
Me	Me	*t*-Bu	**38**	52	t	**43**	31	95

[a] Isolated yields, based on starting phosphine, of products obtained by fractional distillation. t = trace (i.e. product not isolated by distillation but detected by ^{31}P NMR in the reaction mixture).

Reaction of 17 with CCl_4. The reaction was carried out as described in parts a and b above, but upon attempted distillation only a few drops of **30** (Tables I and II) was distilled. The residue in the flask was dissolved in CH_2Cl_2, crystallized by adding hexane, and identified as oligomeric $\{[CH_2{=}CHCH(SiMe_3)]P(Ph){=}N\}_n$ by ^{31}P NMR (δ −5.42) and elemental analysis. Anal. Calcd: C, 61.24; H, 7.71. Found: C, 61.62; H, 6.70.

Reaction of 1 and 2 with CCl_4. The reaction of **1** with CCl_4 was carried out as described in parts a and b above and also according to procedure b with freshly distilled hexane as a solvent. In each case as many as four major signals and several smaller signals were observed in the ^{31}P NMR spectra of the reaction mixtures. Vacuum distillation did not give any fractions containing a single pure compound. However, low yields of pure samples of **44** and **45** were obtained in dilute CH_2Cl_2 solutions. Typically, phosphine **1** (7.23 g, 32.7 mmol) and CH_2Cl_2 (32 mL) were placed in a 250-mL round-bottom flask equipped with a magnetic stirrer, nitrogen inlet, and addition funnel. After the solution was cooled to 0 °C, CCl_4 (3.2 mL, 32.7 mmol) in CH_2Cl_2 (32 mL) was added dropwise. The mixture was warmed to room temperature and stirred for ca. 1 h. Solvent removal and distillation afforded **44**. A similar procedure using ca. twice as much CH_2Cl_2 was used to obtain **45**.

Thermal Decomposition of 46. A sample (3.95 g, 12.8 mmol) of **46** was placed in a heavy-walled glass ampule that was sealed under vacuum. Light brown solids formed after heating in an oven at 180 °C for 67 h. The ampule was opened, and Me_3SiCl (1.38 g, yield 97%) was removed under vacuum. A ^{31}P NMR spectrum of the crude material contained a large signal at δ 15.24 and a small one at δ 6.12. Recrystallization from hot CH_3CN gave pure crystals of the trimer $(Ph_2P{=}N)_3$ (mp 228–230 °C; ^{31}P (THF) δ 15.9).[20]

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Supplementary Material Available: Tables of ^1H and ^{13}C NMR spectroscopic data and analytical data for all new compounds (15 pages). Ordering information is given on any current masthead page.

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(20) Allcock, H. R. "Phosphorus-Nitrogen Compounds"; Academic Press: New York, 1972.

Contribution from the Laboratoire des Acides Minéraux, Université des Sciences et Techniques du Languedoc, 34060 Montpellier Cédex, France, Laboratoire de Physicochimie Structurale, Université de Paris Val de Marne, 94000 Créteil, France, and LURE,[1a] Université de Paris-Sud, 91405 Orsay, France

Structural Approach to the Behavior of ClO_4^- as a Ligand in Transition-Metal Complexes Using EXAFS, IR, and Raman Spectroscopy. 1. A Perchlorate-Bridged Copper Chain with Short Copper–Copper Distances in $Cu(ClO_4)_2$

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A new synthetic route has been applied to the preparation of anhydrous copper perchlorate and a combined study including extended X-ray absorption fine structure (EXAFS), infrared, and Raman spectroscopies used in an effort to determine the mode of coordination about copper. Oxygen atoms of the perchlorate groups form a square-planar environment around copper, with a short (1.96 Å) Cu–O distance, while oxygen atoms at a longer distance (2.68 Å) complete its coordination shell. The best agreement in the treatment of the EXAFS data is obtained by including a copper–copper contribution to the second coordination shell, so it is proposed that the perchlorate groups bridge two coppers, forming infinite chains. In one of these, the inter-copper distance is remarkably short (3.01 Å). However, no magnetic coupling has been found from either ESR or magnetic measurements between the two copper centers.

Until quite recently little information concerning the coordinating ability of the perchlorate group to metal ions was available in the literature.[2] Among the early studies is the work of Hathaway,[3] who recognized the presence of bidentate perchlorate in $Cu(ClO_4)_2$.

During the past decade, new synthetic methods have allowed the preparation of a series of perchlorato complexes of transition and non transition metals.[4,5] Unfortunately, such compounds exhibit a violent reactivity that limits considerably their manipulation. In particular, this reactivity prevents the employment of the solvents usual in crystal growth. For this reason, a solid product is frequently obtained in the form of a polycrystalline powder so that most of the structural data available to date have been obtained from vibrational spectroscopic studies. However, recent attempts to grow single crystals of perchlorato complexes of tin[6] and antimony[7] using $SbCl_5$ and $SnCl_4$ as solvents have been successful and have allowed their full structure determination by X-ray diffraction.

Extended X-ray absorption fine structure (EXAFS) is a powerful technique particularly well adapted to the structural study of polycrystalline powders, giving radial distances and information about the type and number of scattering atoms

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(2) Rosenthal, M. R. *J. Chem. Educ.* **1973**, *50*, 331. Schilt, A. A. in "Perchloric Acid and Perchlorates"; G. Frederick Smith Chemical Co.: Columbus, OH 1979; p 46.

(3) Hathaway, B. J.; Underhill, A. E. *J. Chem. Soc.* **1961**, 3091.

(4) (a) Chaabouni, M.; Pascal, J. L.; Pavia, A. C.; Potier, J.; Potier, A. *C. R. Hebd. Seances Acad. Sci., Ser. C* **1978**, *287*, 41. (b) Chaabouni, M.; Pascal, J. L.; Potier, J. *Ibid.* **1980**, 291, 125. (c) Loginov, S. R.; Nikitina, Z. K.; Rosolovskii, V. Ya. *Russ. J. Inorg. Chem.* (*Engl. Transl.*) **1978**, *23*, 178. (d) Loginov, S. R.; Nikitina, Z. K.; Rosolovskii, V. Ya. *Zh. Neorg. Khim.* **1980**, *25*, 1009.

(5) Chaabouni, M.; Pascal, J. L.; Potier, A.; Potier, J. *J. Chem. Res., Synop.* **1977**, *3*, 80. Chaabouni, M.; Chausse, T.; Pascal, J. L.; Potier, J. *Ibid.* **1980**, *3*, 72.

(6) Belin, C.; Chaabouni, M.; Pascal, J. L.; Potier, J.; Rozière, J. *J. Chem. Soc., Chem. Commun.* **1980**, 105.

(7) Belin, C.; Chaabouni, M.; Pascal, J. L.; Potier, J. *Inorg. Chem.* **1982**, *21*, 3557.

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