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Synthesis and NMR Characterization of New Aminomethylenephosphines[1]

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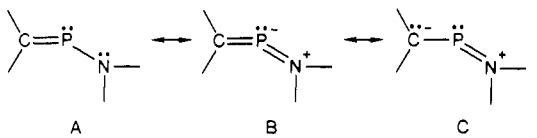
By a variety of synthetic methods, a series of new aminomethylenephosphines, analogous to the known compounds $(Me_3Si)_2NP{=}C(R)SiMe_3$ (**1**, R = H; **3**, R = $SiMe_3$), have been prepared. Treatment of the chlorophosphines $R_2NP(Cl)CH_2SiMe_3$ (**5a**, R = Me; **5b**, R = Et; **5c**, R = *i*-Pr) [prepared from $Me_3SiCH_2PCl_2$ (**4**) and Me_3SiNR_2] with $(Me_3Si)_2NLi$ generally gave separable mixtures of the nucleophilic substitution products $R_2N[(Me_3Si)_2N]PCH_2SiMe_3$ (**6**) and the desired dehydrohalogenation products, the methylenephosphines $R_2NP{=}C(H)SiMe_3$ (**7b**, R = Et; **7c**, R = *i*-Pr). With **5a**, only substitution was observed. Several other aminomethylenephosphines were obtained by chloride displacement from $(Me_3Si)_2C{=}PCl$ (**2**). Thus, **2** reacted readily with Me_3SiNMe_2, *t*-$BuNH_2$, and $R'SiMe_2N(R)Li$ to afford respectively $Me_2NP{=}C(SiMe_3)_2$ (**8**), *t*-Bu(H)NP=$C(SiMe_3)_2$ (**9**), and $R'SiMe_2(R)NP{=}C(SiMe_3)_2$ (**10a**, R = R' = Me; **10b**, R = *t*-Bu, R' = Me; **10c**, R = H, R' = *t*-Bu; **10d**, R = Me, R' = *t*-Bu). The new aminomethylenephosphines **7-10** were characterized by elemental analyses and NMR spectroscopy (^1H, ^{13}C, ^{31}P, and some ^{29}Si). A linear correlation between the ^{31}P chemical shifts and the one-bond phosphorus-carbon coupling constants (J_{PC}) was observed.

Introduction

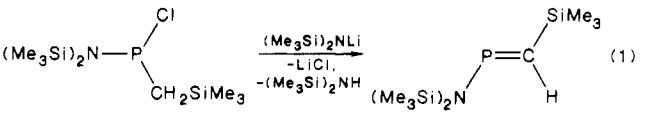
Since the first reports[2] in the late 1970s of the synthesis of stable methylenephosphines or "phosphaalkenes", $RP{=}CR_2$, the preparative chemistry,[3] reactivity,[4] and coordination chemistry[5] of these species have been developed to a considerable extent. The aminomethylenephosphines,[6] in which an amino group is also attached to the sp^2-hybridized phosphorus center, are an interesting subclass of these materials that have received comparatively little attention. The nitrogen "lone pair" electrons can be delocalized into the π system (i.e., resonance forms such as B and C), thus altering the



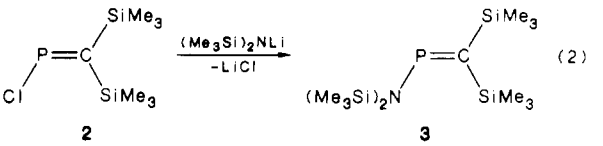
A B C

reactivity and stereochemistry of the P=C double bond. An example of the unusual stereochemistry of aminomethylenephosphines is found in the η^1 complex $(Me_3Si)_2NP[Fe(CO)_4]{=}C(SiMe_3)_2$, which has a dramatic twist (of ca. 30°) in the P=C double bond due to the steric hindrance of the $(Me_3Si)_2N$ group.[7] Moreover, the C=PN linkage makes the aminomethylenephosphines the neutral, isoelectronic analogues of the bis(amino)phosphenium cations, $(R_2N)_2P^+$,[8] which are also of current interest in the realm of "low-coordinate" main-group-element systems.

In this context, recent work in our laboratory has mainly involved the chemistry of the tri- (**1**)[9] and tetrasilylated (**3**)[7] aminomethylenephosphines that bear the bulky bis(trimethylsilyl)amino group, $(Me_3Si)_2N$, on phosphorus. These compounds are prepared respectively by dehydrohalogenation of an appropriate chlorophosphine precursor (eq 1) or by nucleophilic substitution of the chloromethylenephosphine **2** (eq 2). Since our initial reports,[7,9] syntheses of these methylenephosphines by other methods[3b,6c] have appeared in the literature.



(1)



(2)

As a continuation of our studies of aminomethylenephosphines, we report here the synthesis and NMR spectral characterization of several less highly silylated analogues of **1** and **3** that contain alkyl and/or hydrogen substituents on the nitrogen atom. With fewer silyl groups on nitrogen, it should be possible to more directly assess the effects of the π-donor properties of the amino group and to study the chemistry of the P=C double bond without the complicating possibility of Si-N bond cleavage.

Results and Discussion

Analogues of Compound 1. With the objective of preparing *dialkyl*amino analogues of the *disilyl*aminomethylenephosphine **1**, we first synthesized the necessary chlorophosphine precursors **5** by treating [(trimethylsilyl)methyl]dichlorophosphine (**4**, eq 3)[10] with 1 equiv of the appropriate (dialkylamino)silane (eq 4). These

(1) Taken in part from: (a) Thoma, R. J. Ph.D. Dissertation, Texas Christian University, Fort Worth, TX, 1984. (b) Prieto, C. A. M.S. Thesis, Texas Christian University, Fort Worth, TX, 1986.
(2) (a) Becker, G. *Z. Anorg. Allg. Chem.* **1976**, *423*, 242. (b) Kleback, Th. C.; Lourens, R.; Bickelhaupt, F. *J. Am. Chem. Soc.* **1978**, *100*, 4887.
(3) See for example: (a) Appel, R.; Knoll, F.; Ruppert, I. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 731. (b) Niecke, E.; Scholler, W. W.; Wildbredt, D.-A. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 131. (c) Xie, Z.-M.; Wisian-Neilson, P.; Neilson, R. H. *Organometallics* **1985**, *4*, 339. (d) Issleib, K.; Schmidt, H.; Wirkner, C. *Z. Anorg. Allg. Chem.* **1981**, *473*, 85. (e) van der Knaap, Th. A.; Klebach, Th. C.; Visser, K.; Bickelhaupt, F.; Ros, P.; Baerends, E. J.; Stam, C. H.; Konijin, M. *Tetrahedron* **1984**, *40*, 765. (f) Cowley, A. H.; Jones, R. A.; Lasch, J. G.; Norman, N. C.; Stewart, C. A.; Stuart, A. L.; Atwood, J. L.; Hunter, W. E.; Zhang, H.-M. *J. Am. Chem. Soc.* **1984**, *106*, 7015.
(4) See for example: (a) Ford, R. R.; Li, B.-L.; Neilson, R. H.; Thoma, R. J. *Inorg. Chem.* **1985**, *24*, 1993. (b) Appel, R.; Knoch, F.; Zimmermann, R. *Chem. Ber.* **1985**, *118*, 814. (b) Appel, R.; Casser, C. *Tetrahedron Lett.* **1984**, *25*, 4109. (c) Markovskii, L. N.; Romanenko, V. D.; Pidvarko, T. V. *J. Gen. Chem. USSR (Engl. Transl.)* **1984**, *53*, 1502. (d) van der Knaap, Th. A.; Bickelhaupt, F. *Tetrahedron Lett.* **1982**, *23*, 2037.
(5) See for example: (a) Kraaijkamp, J. G.; van Koten, G.; van der Knaap, Th. A.; Bickelhaupt, F.; Stam, C. H. *Organometallics* **1986**, *5*, 2014. (b) Arif, A. M.; Cowley, A. H.; Quashie, S. *J. Chem. Soc., Chem. Commun.* **1985**, 428. (c) Holand, S.; Charrier, C.; Mathey, F.; Fischer, J.; Mischler, A. *J. Am. Chem. Soc.* **1984**, *106*, 826. (d) Cowley, A. H.; Jones, R. A.; Stewart, C. A.; Stuart, A. L. *J. Am. Chem. Soc.* **1983**, *105*, 3737. (e) Kroto, H. W.; Nixon, J. F.; Taylor, M. J.; Frew, A. A.; Muir, K. *Polyhedron* **1982**, *1*, 89.
(6) (a) Appel, R.; Kündgen, U. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 219. (b) Appel, R.; Kündgen, U.; Knoch, F. *Chem. Ber.* **1985**, *118*, 1352. (c) Romanenko, V. D.; Polyachenko, L. K.; Markovskii, L. N. *Phosphorus Sulfur* **1984**, *19*, 189. (d) Romanenko, V. D.; Polyachenko, L. K.; Markovskii, L. N. *Phosphorus Sulfur* **1985**, *22*, 365. (e) Haase, M.; Klingebiel, U.; Skoda, L. *Chem. Ber.* **1984**, *39*, 1500. (f) Romanenko, V. D.; Polyachenko, L. K.; Markovskii, L. N. *J. Gen. Chem. USSR (Engl. Transl.)* **1984**, *54*, 860. (g) Prischchenko, A. A.; Gromov, A. V.; Luzikov, Yu. N.; Borisenko, A. A.; Lazhko, E. I.; Klaus, K.; Lutsenko, I. F. *J. Gen. Chem. USSR (Engl. Transl.)* **1984**, *54*, 1354.
(7) Neilson, R. H.; Thoma, R. J.; Vickovic, I.; Watson, W. H. *Organometallics* **1984**, *3*, 1132.
(8) Cowley, A. H.; Kemp, R. A. *Chem. Rev.* **1985**, *85*, 367.
(9) Neilson, R. H. *Inorg. Chem.* **1981**, *20*, 1969.
(10) Corriu, R. J. P.; Masse, J.; Samati, D. *J. Organomet. Chem.* **1975**, *93*, 71.

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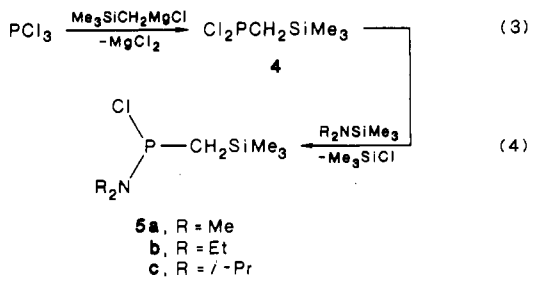
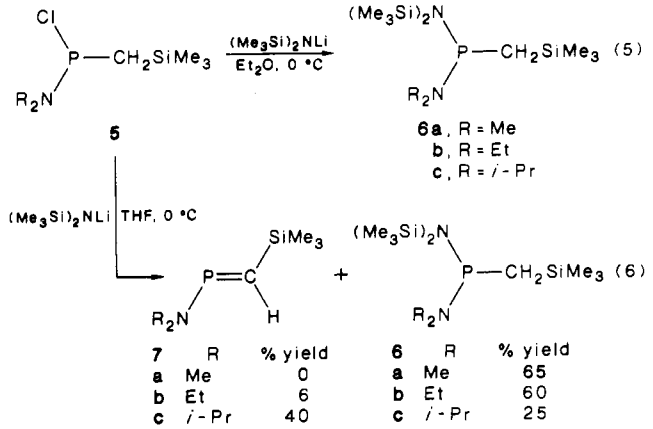


Si–N cleavage reactions proceeded smoothly, and the new aminochlorophosphines **5** were obtained in good yields as air-sensitive, but thermally stable, distillable liquids, which were fully characterized by elemental analyses and NMR (^1H, ^{13}C, and ^{31}P) spectroscopy (Tables I and II).

As part of a study of P–N rotational barriers, Goldwhite and Power[11] have reported the synthesis of aminophosphines similar to **5a** and **5c** that contain the bis(trimethylsilyl)methyl group, $(Me_3Si)_2CH$, instead of the monosilyl moiety Me_3SiCH_2. Their synthetic method was also different in that it involved the reaction of the dichlorophosphines R_2NPCl_2 with $(Me_3Si)_2CHLi$. Recently, we have also prepared a variety of other (silylmethyl)-phosphines[1b,12] as potential condensation precursors to new P–C oligomers.

The chlorophosphines **5** were studied as possible precursors to the (dialkylamino)methylenephosphine analogues of **1**. When **5** was treated with $(Me_3Si)_2NLi$ in Et_2O solution (the same conditions that were used to prepare **1**), only the nucleophilic substitution products **6** were produced (eq 5). The bis(amino)-

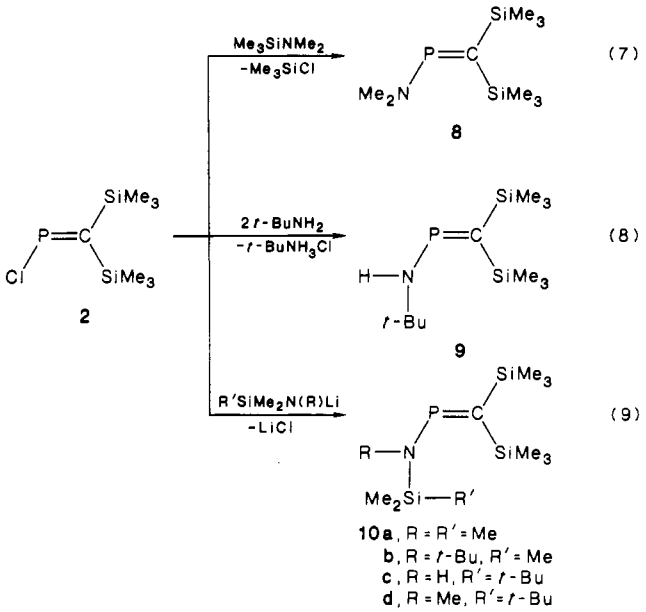


7	R	% yield	6	R	% yield
a	Me	0	a	Me	65
b	Et	6	b	Et	60
c	i-Pr	40	c	i-Pr	25

phosphines **6** were characterized by elemental analysis and NMR spectroscopy (Tables I and II). On the other hand, when the same reactions were carried out in THF (a more basic solvent), dehydrohalogenation to give the desired aminomethylenephosphines **7** (eq 6) occurred along with substitution. The isolated yields of the two types of products, shown in eq 6, indicate that increasing the steric bulk of the dialkylamino group favors the formation of the dehydrohalogenation product **7**. In fact, when R = Me, only substitution is observed. The aminomethylenephosphines **7b** and **7c** were isolated by fractional distillation as colorless liquids that gave satisfactory elemental analyses and NMR spectral data consistent with their proposed structures. The ^{31}P NMR chemical shifts and phosphorus–carbon coupling constants of these and other aminomethylenephosphines are discussed in a later section of this paper.

Efforts to prepare the aminomethylenephosphines **7** in higher yield were generally unsuccessful. The reactions of **5** with a variety of other bases, including $(i\text{-Pr})_2NLi$ and nonnucleophilic amines such as DBU (1,8-diazabicyclo[5.4.0]undec-7-ene) and DBO (1,4-diazabicyclo[2.2.2]octane), were studied. Lithium diisopropylamide gave results very similar to those obtained with $(Me_3Si)_2NLi$, while DBU and DBO generally afforded complex mixtures from which only small and impure quantities of the disproportionation products $(R_2N)_2PCH_2SiMe_3$ could be distilled. Alkyllithium reagents were not tried as possible bases for this process since earlier work[8] had shown that the *disilylamino* precursor to **1** (eq 1) undergoes chloride displacement from phosphorus even with bulky nucleophiles such as *t*-BuLi.

Analogues of 3. Considerably better results were obtained in preparing compounds similar to the [bis(trimethylsilyl)-methylene]phosphine **3**. In this case, it is possible to use a precursor that already contains the P=C double bond, namely the chloromethylenephosphine compound **2**.[13] We find that aminolysis of the P-Cl bond of **2** can be accomplished in three different ways (eq 7–9). These reactions involve, respectively, Si—N bond



cleavage to give the dimethylamino derivative **8**, simple aminolysis with excess *tert*-butylamine to give **9**, and nucleophilic substitution with lithium amides to give the monosilylamino derivatives **10**. All of these aminomethylenephosphines were isolated by fractional distillation as colorless, air-sensitive liquids and were readily characterized by elemental analysis and NMR spectroscopy (Tables I and II). Compound **10b**, in fact, has been prepared previously by Markovskii et al.[6c] by the reaction of $(Me_3Si)_3CLi$ with the iminophosphine $(Me_3Si)_2NP{=}N(t\text{-Bu})$. This latter process occurs via displacement of the $(Me_3Si)_2N^-$ moiety from phosphorus, followed by a migration of a Me_3Si group from carbon to nitrogen.

Appel and co-workers[6a,b] have obtained some related aminomethylenephosphines by treatment of the *C*-phenyl analogue of **2** [i.e., $Me_3Si(Ph)C{=}PCl$] with a few secondary amines (or *t*-$BuNH_2$) in the presence of Et_3N. In some cases, however, they observed side reactions involving addition of the amine R_2NH to the P=C double bond of the methylenephosphine product. This type of reaction, of course, is not possible in aminolyses such as those in eq 7 and 9. Also, it does not occur to an observable extent in the *t*-$BuNH_2$ reaction (eq 8), probably due to the greater steric hindrance afforded by the presence of *two* Me_3Si groups on carbon in compound **9**.

NMR Spectral Data. Generally, the new compounds prepared in this study gave NMR spectra (^1H, ^{13}C, and ^{31}P; Table I) that led to unambiguous assignments of their structures. A curious feature of the ^1H NMR spectra of the precursors **5** and **6**, however, was noted. All six of these (silylmethyl)phosphines contain a chiral phosphorus center and, thus, should exhibit nonequivalence of the diastereotopic silylmethylene protons (PCH_2SiMe_3). In fact, four of these compounds (**5c**, **6a**, **6b**, and **6c**) do exhibit the expected ABX splitting pattern. On the other hand, compounds **5a** and

(11) Goldwhite, H.; Power, P. P. *Org. Magn. Reson.* **1978**, *11*, 499.
(12) Neilson, R. H.; Prieto, C. A., to be submitted for publication in *Phosphorus Sulfur.*
(13) Appel, R.; Westerhaus, A. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 556.

Table I. NMR Spectroscopic Data[a]

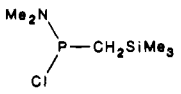
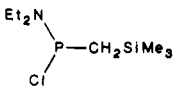
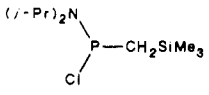
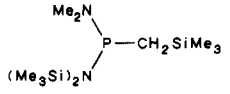
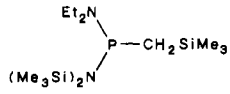
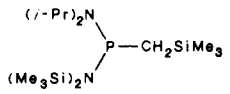
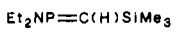
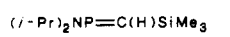
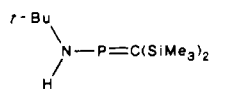
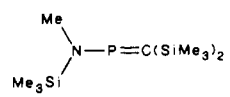
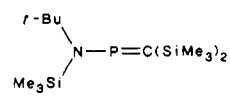
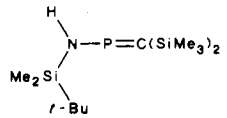
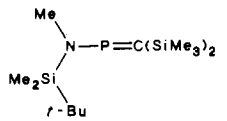
compd	signal	^{1}H NMR δ	^{1}H NMR J_{PH}[c]	^{13}C NMR δ	^{13}C NMR J_{PC}	^{31}P NMR δ
 **5a**	Me_3Si	0.13	0.8	−0.32	4.9	164.6
	PCH_2	1.58	6.0	26.86	46.4	
	NMe_2	2.63	15.0	39.95	10.4	
 **5b**	Me_3Si	0.20	1.5	−0.10	5.5	158.0
	PCH_2	1.58	6.3	26.64	47.6	
	NCH_2	2.9–3.3[b]		43.50	12.2	
	CH_3	1.17	(7.2)	14.23	6.2	
 **5c**	Me_3Si	0.18	1.0	−0.06	5.9	147.0
	PCH_2[d]	1.69	6.5	25.60	49.8	
		1.34	5.1			
			(13.9)			
	NCH	3.9–4.0[b]		47.10	5.9	
	CH_3	1.20	18.0	22.71	5.9	
			(7.6)			
 **6a**	Me_3SiC	0.13	0.6	0.20	6.1	95.7
	Me_3SiN	0.28	1.5	5.34	7.9	
	PCH_2[d]	0.82	4.4	22.30	38.4	
		1.53	2.0			
			(13.9)			
	NMe_2	2.60	10.5	40.57	15.9	
 **6b**	Me_3SiC	0.05	0.8	0.22	6.8	92.6
	Me_3SiN	0.25	1.4	5.42	8.8	
	PCH_2[d]	1.47	4.9	22.03	39.1	
		0.90	2.4			
			(14.0)			
	NCH_2	2.9–3.2[b]		42.20	16.6	
	CH_3	1.06	(7.2)	14.60	2.9	
 **6c**	Me_3SiC	0.16	0.9	0.46	6.8	73.8
	Me_3SiN	0.30	1.2	6.01	8.8	
	PCH_2	0.5–1.2[e]		22.22	41.0	
	NCH	3.4–3.8[b]		46.70	10.7	
	CH_3[d]	1.20	6.9	24.49	9.8	
		1.14	6.9			
			(6.9)			
 **7b**	Me_3Si	0.07	1.2	1.55	8.5	280.3
	NCH_2	3.26	7.1	44.50	12.2	
	CH_3	1.08	(7.1)	15.00	3.0	
	CH	6.00		117.30	57.4	
 **7c**	Me_3Si	0.06	1.2	1.79	8.5	273.2
	NCH	3.82	3.6	47.98	4.3	
	CH_3	1.18	(6.6)	23.90	6.1	
	CH	6.23	16.1	116.30	59.8	
 **8**	Me_3Si	0.08	3.0	3.73	12.7	331.3
		1.10		4.25		
	NMe_2	2.87	6.0	42.72	12.7	
	C=P			129.70	77.2	
 **9**	Me_3Si	0.15	1.7	3.06	3.6	307.5
		0.21		2.87		
	*Me*C	1.29		32.65	7.9	
	Me_3C			47.62		
	C=P			127.30	71.0	
	NH	5.20	12.8			
 **10a**	Me_3SiC	0.23	1.5	3.90	16.1	350.1
		0.22		4.05	4.0	
	Me_3SiN	0.19	2.9	0.26	9.1	
	NMe	2.95	4.4	37.09	10.1	
	C=P			142.65	86.5	
 **10b**	Me_3SiC	0.27		3.65	16.1	392.8
		0.26		3.50	3.0	
	Me_3SiN	0.25		6.10	3.1	
	Me$_3$C	1.40	1.9	33.05	8.1	
	Me_3C			56.70	5.0	
	C=P			182.81	93.6	

Table I (Continued)

compd	signal	^{1}H NMR δ	^{1}H NMR J_{PH}[c]	^{13}C NMR δ	^{13}C NMR J_{PC}	^{31}P NMR δ
 10c	Me_3SiC	0.20[f]		2.90 3.26	14.1	324.1
	Me_2SiN	0.27[f]		3.63		
	Me$_3$C	0.95		36.03		
	Me_3C			26.51		
	C=P			140.06	71.6	
	NH	4.70				
 10d	Me_3SiC	0.21 0.24	2.5	4.03 4.34	16.1	350.2
	Me_2SiN	0.25	2.4	4.30		
	Me$_3$C	0.95		27.01	4.0	
	Me_3C			19.89		
	MeN	3.02	4.4	38.59	10.1	
	C=P			140.59	87.6	

[a] Chemical shifts relative to Me_4Si for ^{1}H and ^{13}C spectra and to H_3PO_4 for ^{31}P spectra; coupling constants in Hz. Solvents: $CDCl_3$ or CH_2Cl_2 unless otherwise noted. [b] Complex multiplet. [c] J_{HH} values in parentheses. [d] Diastereotopic protons observed. [e] Obscured by signals due to CH_3 of *i*-Pr group. [f] Broad, overlapping signals.

Table II. Preparative and Analytical Data

compd	yield, %	bp, °C (mm Hg)	anal.,[a] % C	anal.,[a] % H
5a	82	43–46 (0.1)	36.45 (36.61)	8.67 (8.75)
5b	85	54–58 (0.15)	42.56 (42.64)	9.37 (9.48)
5c	50	51–53 (0.01)	47.20 (47.32)	10.17 (9.93)
6a	65	75–77 (0.2)	44.82 (44.67)	10.95 (10.93)
6b	60	75–78 (0.01)	47.84 (47.95)	11.06 (11.21)
6c	25	82–85 (0.05)	50.53 (50.74)	11.50 (11.44)
7b	6	23–25 (0.07)	50.75 (50.76)	10.35 (10.65)
7c	40	24–27 (0.05)	55.04 (55.26)	11.38 (11.13)
8	75	64–67 (0.5)	45.16 (46.31)	10.48 (10.36)
9	54	68–75 (0.02)	50.30 (50.54)	10.99 (10.72)
10a	36	63–67 (0.03)	44.89 (45.19)	10.20 (10.53)
10c	28	92–100 (0.05)	48.88 (48.90)	10.43 (10.65)
10d	62	92–94 (0.1)	48.76 (50.41)[b]	10.91 (10.81)

[a] Calculated values in parentheses. [b] Minor (ca. 5%) inseparable impurities present.

5b show only a simple doublet for their PCH_2Si protons. This is probably not due to an accidental chemical shift equivalence because it is observed on a 300-MHz instrument for samples in a variety of solvents. Since P–N–C and P–N–C–H spin couplings are observed, the process by which the PCH_2Si protons are rendered equivalent on the NMR time scale cannot involve P–N bond cleavage. The most reasonable explanation is a rapid intermolecular chloride exchange, possibly caused by traces of ammonium salts, $R_2NH_2^+Cl^-$, present in the R_2NSiMe_3 reagents. This type of exchange, which would effectively cause loss of stereochemistry at phosphorus, is not possible for compounds **6** and is probably greatly retarded by the steric congestion in the (diisopropylamino)chlorophosphine **5c**.

The aminomethylenephosphines **7b** and **7c** have an unsymmetrical substitution pattern about the P=C double bond and, thus, could potentially exhibit structural isomers. Their NMR spectra, however, clearly indicate the presence of only a single isomer (presumably, the thermodynamic one since the products were heated to ca. 70 °C during distillation) in each case. On the basis of the observation of relatively large spin couplings

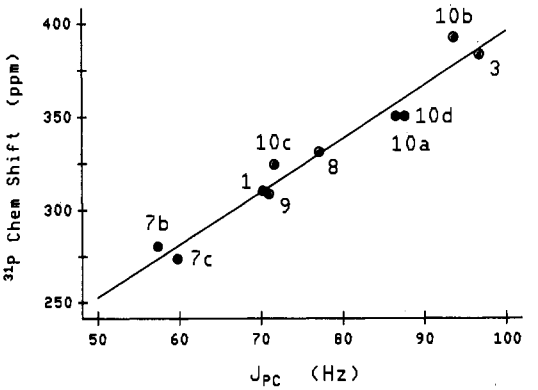
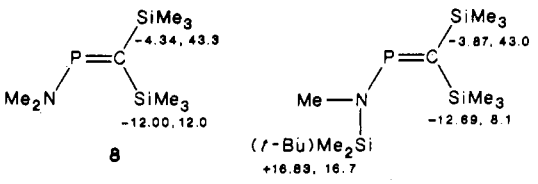


Figure 1. Plot of ^{31}P chemical shifts vs. the one-bond phosphorus–carbon coupling constants (J_{PC}) for the aminomethylenephosphines **1**,[8] **3**,[9] and **7–10** (correlation coefficient 0.975).

between phosphorus and the Me_3Si protons ($^4J_{PH}$ = 1.2 Hz) and carbons ($^3J_{PC}$ = 8.5 Hz), we assign the structure to be that shown in eq 6 in which the Me_3Si group lies in a cis relationship to the phosphorus lone pair.[14] This is the sterically least crowded arrangement and is the one adopted by most other known aminomethylenephosphines.[6] Indeed, a trans orientation of the amino and silyl groups has been confirmed by an X-ray diffraction study of the close analogue $Me_2NP{=}C(Ph)SiMe_3$.[6a]

For some of the new aminomethylenephosphines, we also recorded ^{29}Si NMR spectra. Some typical data [$\delta(^{29}Si)$; J_{PSi} Hz] obtained for compounds **8** and **10d** is summarized as follows:



The important point to be made is that, as previously noted for the analogues **1**[3b] and **3**,[9] there are distinct differences in the ^{29}Si chemical shifts and J_{PSi} values for the two Me_3Si groups attached to carbon. The larger P–Si coupling is most reasonably assigned to the Me_3Si group that is cis to the lone pair on phosphorus.[14]

A close inspection of the ^{31}P and ^{13}C NMR spectral data obtained for this series of aminomethylenephosphines revealed

(14) Fluck, E.; Heckmann, G. In *Phosphorus-31 NMR Spectroscopy in Stereochemical Analysis*; Verkade, J. G., Quin, L. D., Eds.; Methods in Stereochemical Analysis; VCH: Deerfield Beach, FL, 1987; Vol. 8, Chapter 2.

an interesting linear correlation (Figure 1) between the ^{31}P chemical shifts and the one-bond J_{PC} values. Generally, as the steric bulk of the amino substituent and/or the number of silyl groups on the carbon end of the P=C double bond increase, the ^{31}P resonance moves downfield and the J_{PC} value increases. While the factors that affect the magnitude of P–C couplings are not well-understood, especially when π bonding is involved,[14] the observed trend in the ^{31}P shifts can be more easily rationalized. Other things being equal, silylation at carbon accentuates the polarity ($C^{\delta-}$–$P^{\delta+}$) of the P=C double bond,[3c,14] thus deshielding the phosphorus and causing a shift to lower field (i.e., higher δ value). Deshielding at phosphorus is also observed when the steric bulk of the substituents on nitrogen is increased. Very bulky amino groups [e.g., $Me_3Si(t\text{-Bu})N$] are probably rotated out of the Si_2C=P plane such that the possibility of P—N π bonding is eliminated. The most sterically hindered aminomethylenephosphines (e.g., **3** and **10b**), therefore, have the most downfield ^{31}P chemical shifts. Similar factors appear to influence the ^{31}P chemical shifts of the isoelectronic bis(amino)phosphenium cations.[7]

Experimental Section

Materials and General Procedures. The following reagents were obtained from commerical sources and used without further purification: *n*-BuLi, Me_3SiCl, Me_3SiCH_2Cl, Me_3SiNMe_2, $(Me_3Si)_2NH$, PCl_3, DBO (1,8-diazabicyclo[5.4.0]undec-7-ene), DBO (1,4-diazabicyclo[2.2.2]octane), and t-$BuNH_2$. Tetrahydrofuran was distilled from Na/benzophenone, and other solvents (Et_2O, CH_2Cl_2, and hexane) were distilled from CaH_2 prior to use. The starting materials, Me_3SiNR_2(R = Et, *i*-Pr),[15] $Me_3SiN(R)H$ (R = Me, *t*-Bu),[15] t-$BuSiMe_2N(R)H$ (R = H, Me),[16] $Me_3SiCH_2PCl_2$ (**4**),[10] $(Me_3Si)_2CHPCl_2$,[17], and $(Me_3Si)_2C$=PCl (**2**),[13] were prepared according to the published procedures. Proton, $^{13}C\{^1H\}$, and $^{29}Si\{^1H\}$ NMR spectra were recorded on a Varian XL-300 spectrometer; $^{31}P\{^1H\}$ NMR spectra were obtained on a JEOL FX-60 instrument. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, NY. All reactions and other manipulations were carried out under an atmosphere of dry nitrogen or under vacuum. The following procedures are typical of those used for the synthesis of the new compounds prepared in this study.

Preparation of (Dialkylamino)[(trimethylsilyl)methyl]chlorophosphines (5). In a typical experiment, Me_3SiNMe_2 (20 mL, 0.012 mol) was added slowly via syringe at 0 °C to a magnetically stirred solution of $Me_3SiCH_2PCl_2$ (**4**); 22.6 g, 0.120 mol) in Et_2O (50 mL). The mixture was allowed to warm to room temperature and was stirred for 3 h. A small amount of white precipitate (probably Me_2NH_2Cl) was removed by filtration, and the solvent was removed under reduced pressure. Distillation under reduced pressure through a 10-cm column afforded **5a** as a pale yellow liquid (Tables I and II). Compounds **5b** and **5c** were prepared in the same manner from **4** and the appropriate silylamine, Me_3SiNR_2.

Reaction of 5 with $(Me_3Si)_2NLi$ in Et_2O. Preparation of [Bis(trimethylsilyl)amino](dialkylamino)[(trimethylsilyl)methyl]phosphines (6). The chlorophosphine **5** (100 mmol) was added at 0 °C via syringe to a stirred solution of $(Me_3Si)_2NLi$ [prepared from $(Me_3Si)_2NH$ (21.7 mL, 104 mmol) and *n*-BuLi (80 mL, 1.3 M in hexane)] in Et_2O (100 mL). After the mixture was stirred overnight at room temperature, the white solid (LiCl) that had formed was removed by filtration. After solvent removal, distillation afforded **6** as a pale yellow liquid in 25–65% yield depending on the substituent at nitrogen (Tables I and II).

Reaction of 5 with $(Me_3Si)_2NLi$ in THF. Preparation of (Dialkylamino)[(trimethylsilyl)methylene]phosphines (7). As above, the chlorophosphine **5c** (9.6 g, 38 mmol) was added at 0 °C via syringe to a stirred solution of $(Me_3Si)_2NLi$ (38 mmol) in THF (125 mL). After the mixture was stirred overnight at room temperature, the mixture was filtered and the solvent was removed under reduced pressure. Fractional distillation through a 10-cm column afforded both **7c** (25% yield) and **6c** (40% yield). Similarly, treatment of **5b** with $(Me_3Si)_2NLi$ in THF gave a separable mixture of **7b** (6%) and **6b** (60%). In the case of **5a** (R = Me), only **6a** was obtained (Tables I and II).

Preparation of (Dimethylamino)[bis(trimethylsilyl)methylene]phosphine (8). The silylamine Me_3SiNMe_2 (20.2 mL, 127 mmol) was added via syringe to a stirred solution of $(Me_3Si)_2C$=PCl (**2**); 28.5 g, 127 mmol) at 0 °C. The mixture was stirred for 2 h, and the solvent and Me_3SiCl were removed under reduced pressure. Distillation gave the methylenephosphine **8** as a yellow liquid (Tables I and II).

Preparation of (*tert*-Butylamino)[bis(trimethylsilyl)methylene]phosphine (9). The chloromethylenephosphine **2** (2.3 g, 14 mmol) was added via syringe to a stirred solution of t-$BuNH_2$ (2.06 g, 28 mmol) in hexane (25 mL) at −78 °C. The mixture was stirred at −78 °C for 30 min and was then allowed to warm to room temperature. Following filtration and solvent removal, distillation afforded **9** as a slightly yellow liquid (Tables I and II).

Preparation of [(Dimethylalkylsilyl)amino][bis(trimethylsilyl)-methylene]phosphines (10). A 100-mL flask, equipped with a magnetic stirrer, was charged with the silylamine t-$BuSiMe_2N(Me)H$ (5.08 g, 35 mmol) and Et_2O (50 mL). After the solution was cooled to 0 °C, *n*-BuLi (13.5 mL, 2.6 M in hexane) was added. The mixture was allowed to warm to room temperature, stirred for 30 min, and then cooled to −78 °C. The chloromethylenephosphine **2** (7.9 g, 35 mmol) was added via syringe, and the mixture was stirred for ca. 2 h while it warmed slowly to room temperature. Filtration, solvent removal, and distillation afforded **10d** as a pale yellow liquid (Talbes I and II). Unidentified minor impurities (ca. 5% by ^1H NMR integration) were not removed by a second distillation through a 10-cm column. Compounds **10a**, **10b**, and **10c** were prepared from **2** and the corresponding silylamides according to the same procedure (Tables I and II).

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

Registry No. **2**, 79454-85-6; **4**, 18148-58-8; **5a**, 111283-32-0; **5b**, 112599-01-6; **5c**, 112599-02-7; **6a**, 90413-60-8; **6b**, 99642-69-0; **6c**, 112599-03-8; **7b**, 112599-04-9; **7c**, 110562-29-3; **8**, 112599-05-0; **9**, 112474-49-4; **10a**, 112599-06-1; **10b**, 89982-44-5; **10c**, 112599-07-2; **10d**, 112599-08-3; Me_3SiNMe_2, 2083-91-2; Me_3SiNEt_2, 996-50-9; $Me_3SiN(Pr\text{-}i)_2$, 17425-88-6; $(Me_3Si)_2NLi$, 4039-32-1; t-$BuNH_2$, 75-64-9; t-$BuSiMe_2N(Me)H$, 61012-64-4; $Me_3SiN(Me)H$, 16513-17-0; $Me_3SiN(Bu\text{-}t)H$, 5577-67-3; t-$BuSiMe_2NH_2$, 41879-37-2.

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(17) Ford, R. R.; Neilson, R. H. *Polyhedron* **1986**, *5*, 643.