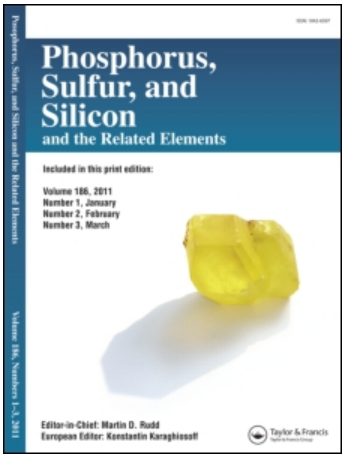


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

SYNTHESIS AND NMR CHARACTERIZATION OF P-VINYL SUBSTITUTED PHOSPHAZENE PRECURSORS[1]

Kenneth E. Waters[a]; Robert H. Neilson[a]
[a] Department of Chemistry, Texas Christian University, Fort Worth, Texas

To cite this Article Waters, Kenneth E. and Neilson, Robert H.(1988) 'SYNTHESIS AND NMR CHARACTERIZATION OF P-VINYL SUBSTITUTED PHOSPHAZENE PRECURSORS[1]', Phosphorus, Sulfur, and Silicon and the Related Elements, 39: 3, 189 — 197
To link to this Article: DOI: 10.1080/03086648808072874
URL: http://dx.doi.org/10.1080/03086648808072874

Phosphorus and Sulfur, 1988, Vol. 39, pp. 189–197
Reprints available directly from the publisher
Photocopying permitted by license only

SYNTHESIS AND NMR CHARACTERIZATION OF P-VINYL SUBSTITUTED PHOSPHAZENE PRECURSORS[1]

KENNETH E. WATERS and ROBERT H. NEILSON*
Department of Chemistry, Texas Christian University, Fort Worth, Texas 76129

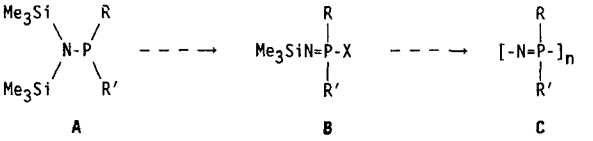
(Received April 22, 1988)

The reactions of either $PhPCl_2$ or PCl_3 with $(Me_3Si)_2NLi$ followed by $H_2C{=}CHMgBr$ were used to prepare the new P-vinyl substituted [bis(trimethylsilyl)amino]phosphines, $(Me_3Si)_2NP(R)CH{=}CH_2$ [**1**: R = Ph, **2**: $CH{=}CH_2$, **3**: R = Me, and **4**: $R = N(SiMe_3)_2$]. Oxidative bromination of phosphines **1–3** afforded the P-bromo-P-vinyl-N-(trimethylsilyl)phosphoranimines, $Me_3SiN{=}P(CH{=}CH_2)(R)Br$ [**5**: R = Ph, **6**: $R = CH{=}CH_2$, **7**: R = Me], which, upon treatment with CF_3CH_2OH/Et_3N, were subsequently converted to the P-trifluoroethoxy derivatives, $Me_3SiN{=}P(CH{=}CH_2)(R)OCH_2CF_3$ [**8**: R = Ph, **9**: $R = CH{=}CH_2$, **10**: R = Me]. Compounds **1–10**, which are of interest as potential precursors to P-vinyl substituted poly(phosphazenes), were fully characterized by elemental analyses (except for the thermally unstable P-Br derivatives **5–7**) and NMR spectroscopy (^1H, ^{13}C, and ^{31}P) including complete analysis of the vinylic proton splitting patterns via HOM2DJ experiments.

Key words: Phosphazene; (silylamino)phosphine; phosphoranimine; N-silylphosphoranimine; vinyl-substituted; two-dimensional NMR.

INTRODUCTION

A relatively new class of inorganic polymers, the poly(alkyl/arylphosphazenes), $[R_2PN]_n$, in which all of the substituents are attached via P-C bonds, are readily prepared by condensation reactions of appropriate Si–N–P precursors (Equation 1).[2,3]



(1)

More recent efforts have been aimed at expanding the overall scope of this polymerization method by three general approaches. First, Wisian-Neilson and coworkers[4–6] have shown that the P-methyl groups in the preformed polymers (**C**) such as $[Ph(Me)PN]_n$ can be deprotonated by treatment with *n*-BuLi. Subsequent reactions of the polymeric anion intermediate with various electrophiles have produced silyl[4], ferrocenyl[5], and alcohol[6] functionalized poly(alkyl/aryl-phosphazenes). Second, analogous deprotonation/substitution reactions have been carried out on the immediate polymer precursors (**B**) yielding, for example, silyl[7] and phosphinyl[8] substituted N-silylphosphoranimines.

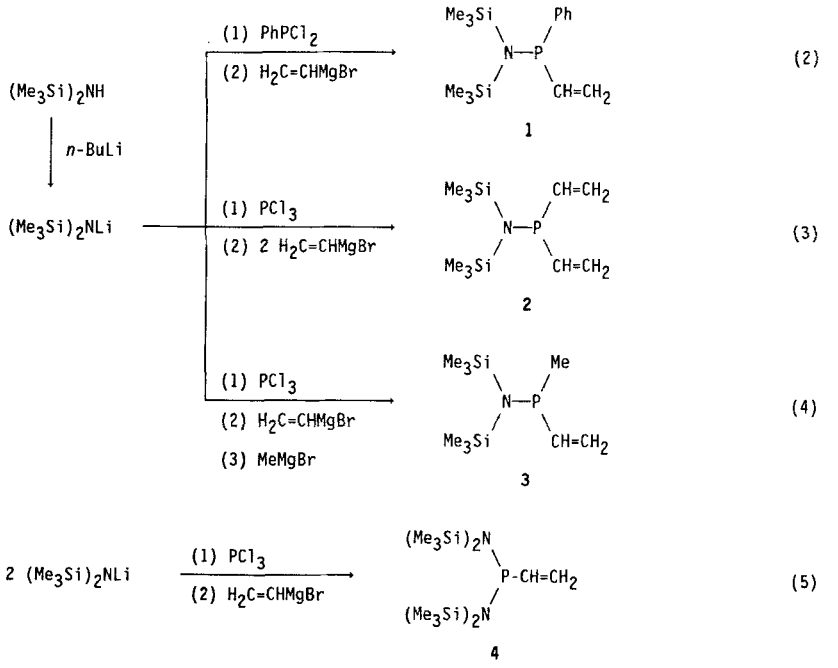
This study is related to the third derivatization method which involves introduction of the desired substituents at the phosphine stage (**A**). In particular, we report

here the synthesis and detailed NMR characterization of a series of new (silylamino)phosphines (**A**) and N-silylphosphoranimines (**B**) which contain vinyl groups on phosphorus. Such compounds are of interest for the eventual preparation of poly(alkyl/arylphosphazenes) bearing *P*-vinyl groups for the purpose of controlled crosslinking of the polymer chains as will be reported elsewhere.

RESULTS AND DISCUSSION

(Silylamino)phosphines

(Disilylamino)phosphines of general formula $(Me_3Si)_2NPR_2$ are conveniently prepared by a "one-pot" synthesis known as the Wilburn method.[9] In this approach, a solution of lithium bis(trimethylsilyl)amide is allowed to react with PCl_3 followed by two equivalents of an alkyl Grignard reagent to yield a phosphine with two identical substituents. Alternatively, reaction of the silylamide with $PhPCl_2$ and one equivalent of an alkyl Grignard affords a phenyl/alkyl substituted (silylamino)phosphine. We have now extended this general approach to include the use of commercial solutions of vinylmagnesium bromide and, thereby, have prepared four new (silylamino)phosphines (**1–4**) containing the vinyl group on phosphorus (Equations 2–5).



The P-vinylphosphines **1–4** are colorless, air-sensitive, distillable liquids that were characterized by elemental analysis (Table I) and NMR spectroscopy (see Table II and discussion below). The formation of the methyl/vinyl-phosphine **3** is

TABLE 1

Preparative and analytical data for P-vinyl phosphines, $(Me_3Si)_2N—P(R)—CH=CH_2$, (**1–4**), and phosphoranimines, $Me_3SiN=P(OCH_2CF_3)(R)—CH=CH_2$ (**8–10**).

Compound	Yield %	bp °C/mm Hg	Analysis[a] %C	%H
1 (R = Ph)	75	79–81/0.05	57.22 (56.90)	9.00 (8.87)
2 (R = CH=CH$_2$)	62	40–43/0.2	49.19 (48.93)	10.16 (9.86)
3 (R = Me)	53	36–39/0.2	45.76 (46.31)	10.38 (10.36)
4 [R = N(SiMe$_3$)$_2$]	45	61–65/0.01	44.52 (44.40)	10.46 (10.38)
8 (R = Ph)	65	56–58/0.15	48.50 (48.59)	5.74 (5.96)
9 (R = CH=CH$_2$)	45	42–45/2.5	39.87 (39.85)	6.32 (6.32)
10 (R = Me)	45	53–56/6.0	36.99 (37.06)	7.17 (6.61)

[a] Calculated values in parentheses.

TABLE II

NMR spectroscopic data.[a]

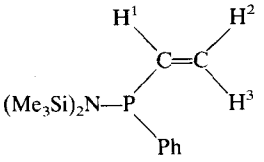
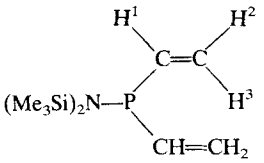
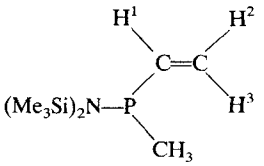
Compound	Signal	^{1}H NMR δ	^{1}H NMR J_{PH}	^{13}C NMR δ	^{13}C NMR J_{PC}	^{31}P NMR δ
 **1**	Me_3Si	0.28	1.0	4.45	5.1	44.3
	CH^1	6.90	11.4 (12.5, 18.5)[b]	144.78	18.1	
	CH^2	5.97	35.4 (2.0)[c]	121.33	4.0	
	CH^3	5.89	13.5			
	Ph	6.8–7.6[d]		127–128[d]		
 **2**	Me_3Si	0.22	1.5	4.38	6.8	40.2
	CH^1	6.50	25.5 (12.8, 18.6)[b]	142.40	23.2	
	CH^2	5.63	25.5 (2.0)[c]	122.60	20.1	
	CH^3	5.50	9.9			
 **3**	Me_3Si	0.19	1.3	4.54	8.8	34.1
	CH_3	1.38	5.7	16.83	23.0	
	CH^1	6.48	23.9 (12.6, 18.7)[b]	145.66	25.5	
	CH^2	5.52	20.8 (1.9)[c]	120.48	14.3	
	CH^3	5.32	8.8			

TABLE II (*continued*)

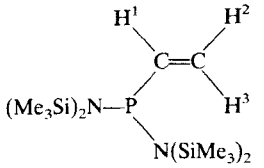
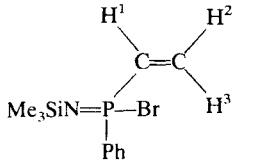
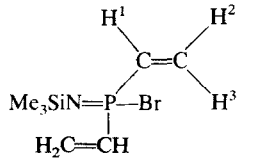
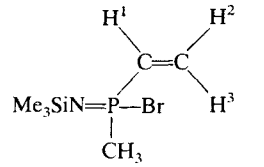
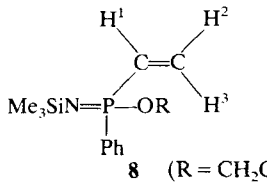
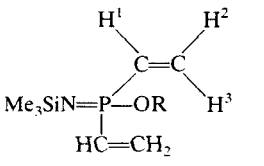
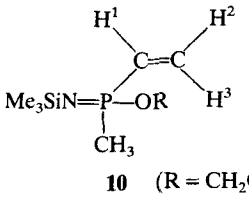
Compound	Signal	^{1}H NMR δ	^{1}H NMR J_{PH}	^{13}C NMR δ	^{13}C NMR J_{PC}	^{31}P NMR δ
 **4**	Me_3Si	0.32		5.76	6.7	95.9
	CH^1	6.82	24.1 (12.1, 18.4)[b]	146.32	39.8	
	CH^2	5.67	34.4 (1.9)[c]	122.76	29.2	
	CH^3	5.61	10.0			
 **5**	Me_3Si	0.19		3.05	6.2	−7.4[e]
	CH^1	6.65	11.6 (12.1, 18.1)[b]	136.04	128.0	
	$CH^{2,3}$	5.9–6.3[d]		f		
	Ph	7.4–7.9[d]		128–132[d]		
 **6**	Me_3Si	0.22		2.60	6.1	12.4[e]
	CH^1	6.35	17.6 (11.7, 18.1)[b]	135.01	112.8	
	$CH^{2,3}$	5.8–6.4[d]		128.05	15.3	
 **7**	Me_3Si	0.20		4.37	7.0	−4.5[e]
	CH_3	2.22	15.0	27.03	75.0	
	CH^1	6.48	23.8 (12.5, 18.8)[b]	136.64	101.3	
	CH^2	5.62	48.4 (1.9)[c]	120.40	14.2	
	CH^3	5.33	8.8			
 **8** (R = CH_2CF_3)	Me_3Si	0.15		3.65	3.0	10.4
	CH^1	6.27	24.5 (12.0, 18.0)[b]	132.30	129.4	
	CH^2	6.00	46.6 (2.2)	132.80	2.8	
	CH^3	6.10	25.5			
	CH_2CF_3	4.1–4.3[d]		59.70	4.5 (34.2)[g]	
	CH_2CF_3			123.80	10.0 (277.0)[g]	
	Ph	7.4–7.9[d]		128–132[d]		
 **9** (R = CH_2CF_3)	Me_3Si	0.20	3.65	3.0	9.1	
	CH^1	5.8–6.2[d]	131.50	120.6		
	$CH^{2,3}$	5.8–6.2[d]	133.42	1.8		
	CH_2CF_3	4.0–4.2[d]	59.58	4.6 (36.0)[g]		
	CH_2CF_3		123.47	8.5 (277.5)[g]		

TABLE II (*continued*)

Compound	Signal	^{1}H NMR δ	^{1}H NMR J_{PH}	^{13}C NMR δ	^{13}C NMR J_{PC}	^{31}P NMR δ
	Me_3Si	0.08		3.64	3.0	21.6
	CH_3	1.42	13.2	17.84	95.9	
	CH^1	6.13	24.8 (11.2, 17.0)[b]	132.43	107.7	
	CH^2	5.95	55.0 (2.0)[c]	133.36	3.8	
	CH^3	5.98	32.2			
10 ($R = CH_2CF_3$)	CH_2CF_3	4.0–4.1[d]		59.37	5.2 (35.9)[g]	
	CH_2CF_3			123.77	8.9 (278.3)[g]	

[a] Chemical shifts relative to Me_4Si for ^{1}H and $^{13}C\{^1H\}$ spectra and to H_3PO_4 for $^{31}P\{^1H\}$ spectra; coupling constants in Hz. Solvents: $CDCl_3$ (^{1}H, ^{13}C) or CH_2Cl_2 (^{31}P) unless otherwise noted.
[b] Vinylic H–H couplings ($^3J_{cis}$, $^3J_{trans}$) in parentheses.
[c] Geminal H–H coupling ($^2J_{HCH}$) in parentheses.
[d] Complex multiplet.
[e] Benzene used as solvent for ^{31}P NMR spectra.
[f] Obscured by phenyl signals.
[g] J_{FC} values in parentheses.

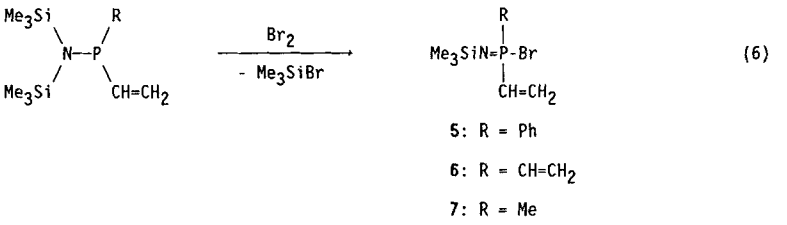
especially significant because prior work in our laboratories had shown that the subsequent combinations of methyl/allyl, methyl/benzyl, and allyl/benzyl could not be prepared by the Wilburn method. The order of addition of the Grignard reagents (i.e., vinyl then methyl) is critical in this case. Although it is clearly formed during the course of the reaction, the intermediate vinylchlorophosphine, $(Me_3Si)_2NP(C)CH{=}CH_2$, could not be isolated from solution without extensive decomposition.

N-Silylphosphoranimines

(Disilylamino)phosphines normally react smoothly with bromine to yield P-bromo-N-silylphosphoranimines via the elimination of Me_3SiBr[10], as opposed to tertiary phosphines R_3P which yield stable phosphonium salts upon bromination. Phosphines **1–3** were, therefore, allowed to react with Br_2 in benzene solution, and in all cases, the corresponding P-bromophosphoranimines were obtained in essentially quantitative yield (Equation 6).

Since most P-bromo-N-silylphosphoranimines are thermally unstable with respect to elimination of Me_3SiBr,[10] compounds **5–7** were not purified by distillation; instead, they were characterized by NMR spectroscopy (Table II) and by their ready conversion to the P-trifluoroethoxyphosphoranimine derivatives as described below. It is interesting to note that, under the conditions studied, the bromination of these vinyl-phosphines occurs exclusively at the phosphorus center rather than the C=C double bond. A similar selectively has been observed previously for some analogous *allyl*(silylamino)phosphines[8] in which the C=C bond is separated from phosphorus by a CH_2 spacer group.

Due to the high reactivity of the P—Br bond, these P-bromo-phosphoranimines are useful for the preparation of various other derivatives including potential poly(phosphazene) precursors. Toward that end, compounds



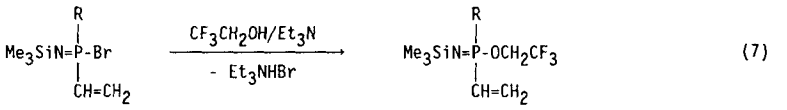
(6)

5: R = Ph

6: R = $CH{=}CH_2$

7: R = Me

5–7 were treated with an equimolar amount of trifluoroethanol in the presence of Et_3N. These reactions afforded the corresponding N-silyl-P-trifluoroethoxyphosphoranimines **8–10** (equation 7) in moderate to good yields. Phosphoranimines **8–10** are all colorless, distillable liquids which gave satisfactory elemental analyses (Table I) and NMR spectra (Table II) that were completely consistent with the proposed structures.



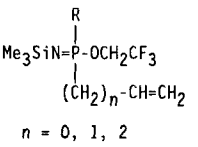
(7)

8: R = Ph

9: R = $CH{=}CH_2$

10: R = Me

Thus, the $H_2C{=}CH$-moiety, introduced via the Grignard reagent at the (silylamino)phosphine stage, was found to be unaffected by the subsequent oxidation with bromine (Equation 6) and nucleophilic substitution with CF_3CH_2OH (Equation 7). The successful preparation of these vinyl substituted phosphoranimines completes the following series of related phosphazene precursors bearing vinyl (i.e., **8–10**), allyl[8], and butenyl[11] functional groups. The thermal decomposition reactions of these precursors and the nature of the polymeric products thus obtained will be described in a future paper.



n = 0, 1, 2

NMR Spectral Data

In addition to the preparative chemistry, a major objective of this study was to assign as completely as possible the NMR spectra of these vinyl systems. The availability and interpretation of such data on the small molecule "monomers" is vital to the eventual characterization of their condensation polymers. Generally, the ^{31}P and ^{13}C NMR spectra of compounds **1–10** were quite straightforward, with chemical shifts and P-C coupling constants typical of those found for related (silylamino)phosphines[8,9,12] and phosphoranimines.[10,11] The ^{13}C NMR spectra

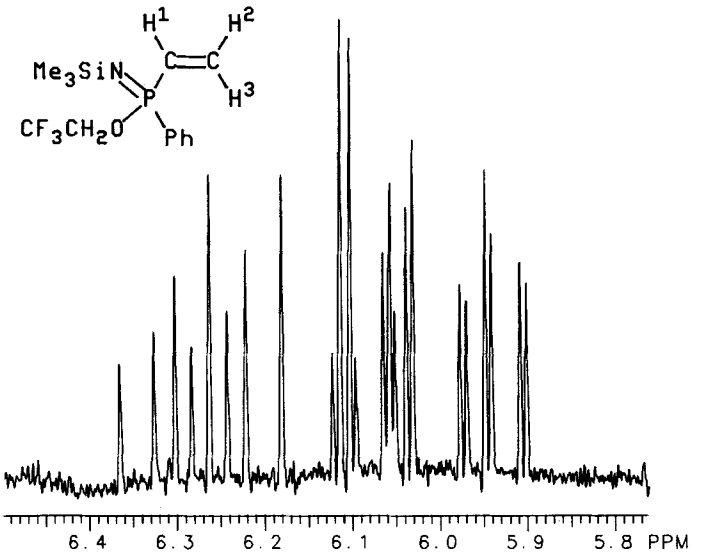


FIGURE 1 Vinylic region of the ^{1}H NMR spectrum (300 MHz) of the P-vinylphosphoranimine **8**.

clearly show the expected[13] differences in the vinyl J_{PC} values between the P^{III} and P^{V} systems. Thus, while the (silylamino)phosphines **1–4** have relatively small couplings (<40 Hz) with similar values for $^1J_{PC}$ and $^2J_{PC}$, the phosphoranimines **5–10** all exhibit large one-bond ($^1J_{PC} > 100$ Hz) and much smaller two-bond ($^2J_{PC} < 20$ Hz) phosphorus-carbon coupling constants. A vinyl group attached directly to phosphorus in a poly(phosphazene) would, therefore, be expected to show a comparable pattern of one large and one small J_{PC} value for the two vinylic carbons.

The interpretation of the vinylic region of the ^{1}H NMR spectra of these compounds was a considerably more difficult task. On a 90 MHz instrument, the splitting patterns were hoplessly second order. At 300 MHz, however, a nearly first order spectrum, with the predicted 8-line doublet/doublet/doublet pattern for each of the three vinyl protons, was generally observed (Figure 1). A clear differentiation between the various proton-proton and proton-phosphorus couplings was accomplished by recording 2-dimensional spectra using the HOM2DJ pulse sequence. This analysis provides a contour plot (e.g., Figure 2) in which the proton chemical shifts and H–H couplings appear along different coordinate axes. Any *phosphorus*-proton couplings that are present merely result in additional doublet splittings along the chemical shift axis to yield, in a practical sense, a phosphorus-decoupled ^{1}H NMR spectrum. Thus, in most cases it was possible to assign the three P–H and three H–H couplings for the vinyl protons (Table II). Noteworthy are the characteristically large[13] couplings between phosphorus and the *trans* proton (H^2), especially for the P^{V} systems (**8–10**) in which $^3J_{PH}$ is ca. 50 Hz. We have recently observed even larger vicinal P–H couplings ($^3J_{PH} \approx$ 85 Hz) in some analogous four membered ring compounds, the phosphacyclobutenes,[14] in which two pathways for spin-spin coupling are present.

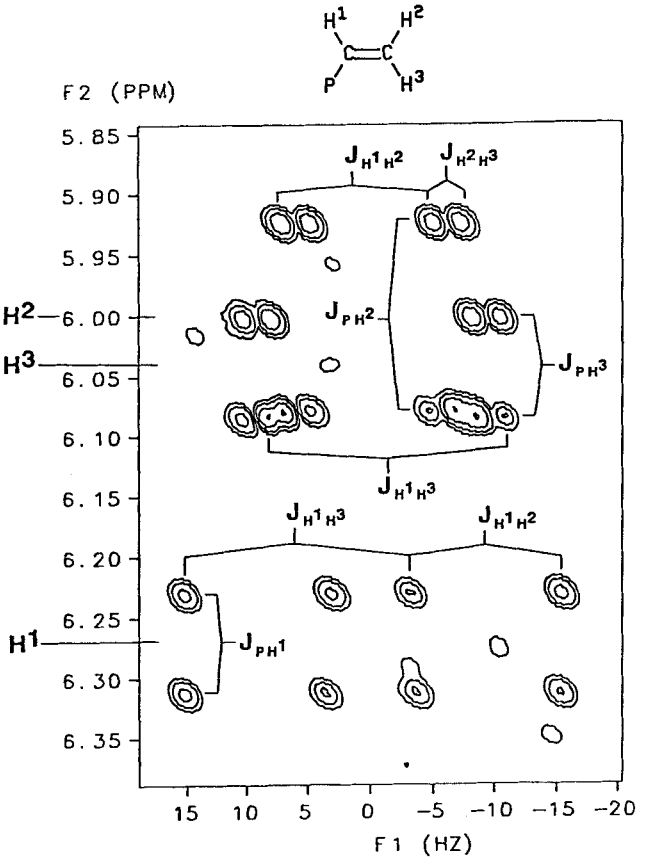


FIGURE 2 Vinylic region of the HOM2DJ ^{1}H NMR spectrum of the P-vinylphosphoranimine **8**.

EXPERIMENTAL SECTION

Materials and General Procedures. The following reagents were obtained from commercial sources and used without further purification: $(Me_3Si)_2NH$, Br_2, PCl_3, $PhPCl_2$, $H_2C{=}CHMgBr$, MeMgBr, and *n*-BuLi. Benzene,[15] ether, hexane, and Et_3N were distilled from CaH_2 and CF_3CH_2OH was distilled from BaO immediately prior to use. Proton and $^{13}C\{^1H\}$ NMR spectra were recorded on a Varian XL-300 spectrometer; $^{31}P\{^1H\}$ NMR spectra were obtained on a JEOL FX-60 instrument. The HOM2DJ spectra were obtained using standard parameters from revision 6.0 of the operating software supplied with the Varian 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 representative of those used for the synthesis of the new compounds prepared in this study.

[*Bis*(*trimethylsilyl*)*amino*](*phenyl*)(*vinyl*)*phosphine* (**1**). In a typical experiment, a 3-L, 3-necked flask, equipped with a mechanical stirrer and a 500-mL addition funnel, was charged with $(Me_3Si)_2NH$ (104 mL, 0.500 mol) and Et_2O (ca. 500 mL). The solution was cooled to 0°C and *n*-BuLi (200 mL, 0.500 mL, 2.5 M in hexane) was added from the addition funnel. This solution was allowed to warm to room temperature and was then stirred for ca. one hour. After rinsing the addition funnel with Et_2O (ca. 20 mL), it was charged with $PhPCl_2$ (67.9 mL, 0.500 mol) which was then added slowly to the stirred reaction mixture at −78°C. The mixture was allowed to warm to room temperature and was then stirred for ca. one hour. The addition funnel was again rinsed with ether and charged with

H_2C=CHMgBr (0.500 mol, 500 mL, 1.0 M in Et_2O). The reaction mixture was cooled to 0°C and the Grignard reagent was added slowly over ca. one hour. The mixture was allowed to warn to room temperature and was stirred for ca. 4 hours. Hexane (ca. 500 mL) was added and the mixture was left overnight without stirring in order to allow the salts to settle. The supernatant solution was decanted through a fritted filter under nitrogen and the salts were washed with two 200-mL portions of hexane. After removal of the solvents under reduced pressure, distillation through a 10-cm column afforded the vinyl-phosphine **1** as a colorless liquid (Tables I and II). The other vinyl[bis(trimethylsilyl)amino]phosphines (**2–4**) were prepared in the same manner from $(Me_3Si)_2NLi$, PCl_3, and H_2C=CHMgBr with appropriate changes in the reaction stoichiometry.

P-Phenyl-P-(trifluoroethoxy)-P-vinyl-N-(trimethylsilyl)phosphoranimine (**8**). A 2-necked flask, equipped with a magnetic stirrer and an addition funnel, was charged with the (disilylamino)phosphine **1** (0.20 mol) and benzene[15] (200 mL). The solution was cooled to 0°C and an equimolar quantity of bromine in benzene (100 mL) was added slowly. After warming to room temperature, the mixture was stirred for ca. one hour. Benzene and Me_3SiBr were removed under reduced pressure. Proton, ^{13}C, and ^{31}P NMR spectra were recorded on the P-bromophosphoranimine **5** (Table II) at this point. Any residual Me_3SiBr was then removed by further exposure of the crude liquid to high vacuum. The bromo derivative **5** was dissolved in fresh benzene (ca. 300 ml) and the solution was transferred to a 3-necked flask, equipped with a mechanical stirrer and an addition funnel. Triethylamine (0.20 mol) was added and the mixture was cooled to 0°C. A solution of CF_3CH_2OH (0.20 mol) in benzene (200 mL) was then added slowly from the addition funnel. The mixture was stirred for ca. 2 hours at room temperature and then filtered under nitrogen. The solids were washed with 2 or 3 portions of hexane. Following solvent removal under reduced pressure, distillation through a 10-cm column afforded the trifluoroethoxy derivative **8** as a colorless liquid (Tables I and II). Compounds **6**, **7**, **9**, and **10** were prepared by means of the same procedures.

ACKNOWLEDGMENT

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

REFERENCES

1. Taken in past from: K. E. Waters, M.S. Thesis, Texas Christian University, Fort Worth, TX, 1986.
2. See for example: (a) R. H. Neilson and P. Wisian-Neilson, *Chem. Rev.*, 1988, **88,** 541. (b) R. H. Neilson; R. Hani, P. Wisian-Neilson, J. J. Meister, A. K. Roy and G. L. Hagnauer, *Macromolecules,* **1987,** 20, 910. (c) R. H. Neilson, R. R. Ford, R. Hani, A. K. Roy, G. M. Scheide, U. G. Wettermark and P. Wisian-Neilson. *ACS Symposium Series,* **1988,** 360, 283.
3. For more general reviews of phosphazene chemistry, see: (a) H. R. Allcock, "Phosphorus-Nitrogen Compounds"; Academic Press, New York, 1972. (b) H. R. Allcock, *Chem. Eng. News* **1985,** 63(11), 22. (c) H. R. Allcock, *ACS Symposium Series,* **1988,** 360, 250. (d) H. R. Allcock, *Angew. Chem., Int. Ed. Engl.* **1977,** 16, 147.
4. P. Wisian-Neilson, R. R. Ford, and R. H. Neilson, A. K. Roy, *Macromolecules* **1986,** 19, 2089.
5. P. Wisian-Neilson and R. R. Ford, *Organometallics* **1987,** 6, 2258.
6. P. Wisian-Neilson, R. R. Ford. *Macromolecules,* in press.
7. U. G. Wettermark, P. Wisian-Neilson, G. M. Scheide, and R. H. Neilson, *Organometallics,* **1987,** 6, 959. For earlier, related work, see: H. Schmidbaur, G. Jonas. *Chem. Ber.* **1967,** 100, 1120.
8. A. K. Roy, R. Hani, R. H. Neilson, P. Wisian-Neilson, *Organometallics* **1987,** 6, 378.
9. (a) R. H. Neilson, P. Wisian-Neilson, *Inorg. Chem.* **1982,** 21, 3568. (b) P. Wisian-Neilson, R. H. Neilson, *Inorg. Synth.*, in press.
10. P. Wisian-Neilson, R. H. Neilson, *Inorg. Chem.* **1980,** 19, 1975.
11. A. K. Roy, U. G. Wettermark, G. M. Scheide, P. Wisian-Neilson, and R. H. Neilson, *Phosphorus and Sulfur* **1987,** 33, 147.
12. B.-L. Li, J. S. Engenito, R. H. Neilson, and P. Wisian-Neilson, *Inorg. Chem.* **1983,** 22, 575.
13. J. G. Verkade, and L. D. Quin, Eds. *Phosphorus-31 NMR Spectroscopy in Stereochemical Analysis*; "Methods in Stereochemical Analysis"; VCH Publishers, Deerfield Beach, Florida, 1987, Vol. 8.
14. B. A. Boyd, R. J. Thomas, and R. H. Neilson, *Tetrahedron Lett.*, **1987,** 28, 6121.
15. Benzene is a potential carcinogen. It should be handled carefully in well-ventilated fume hoods.