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B. A. Boyd and R. H. Neilson

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Synthesis of (1,3-Disilylpropenyl)phosphines[1]

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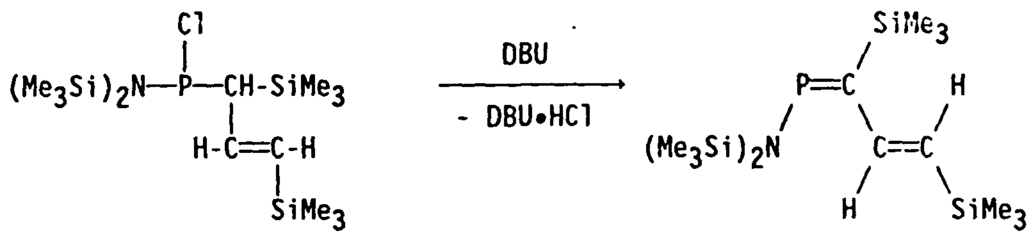
Abstract

A series of the title compounds were generally prepared by the reaction of chlorophosphines RR'PCl (R, R' = Ph, NMe_2) with [1,3-bis(trimethylsilyl)propenyl]lithium. In this manner, the new phosphine derivatives, RR'P[CH($SiMe_3$)CH=CH($SiMe_3$)] (**3**: R = R' = Ph; **4**: R = R' = NMe_2; **5**: R = Ph, R' = NMe_2), were obtained in good yields (ca. 60 - 65%) as thermally stable, distillable liquids. Cleavage of the P-N bonds in **4** by treatment with anhydrous HCl gave the thermally unstable dichloro analogue, Cl_2P[CH($SiMe_3$)CH=CH($SiMe_3$)] (**6**), which did not react cleanly with *t*-BuLi to form (*t*-Bu)(Cl)P[CH($SiMe_3$)CH=CH($SiMe_3$)] (**7**). Instead, compound **7**, a distillable liquid, was obtained in good yield via the direct reaction of the disilyllithium reagent with *t*-BuPCl_2. A small amount of the disubstituted product (*t*-Bu)P[CH($SiMe_3$)CH=CH($SiMe_3$)]$_2$ (**8**) was also produced in the latter reaction. Treatment of the aryl(chloro)(dimethylamino)phosphines, Ar(Me_2N)PCl, with 1,3-disilylpropenyllithium gave either the expected substitution product **9** (Ar = Mes) or a cyclic side product **10** [Ar = 2,4,6-(t-Bu)$_3C_6H_2$] which resulted from dehydrohalogenation of the sterically congested chlorophosphine. The series of disilylamino derivatives, (Me_3Si)$_2$NP(R)[CH($SiMe_3$)CH=CH($SiMe_3$)] (**11**: R = Ph; **12**: R = Me; **13**: R = H), were prepared either by treatment of (Me_3Si)$_2$NP(Ph)Cl with the disilylpropenyllithium reagent (to give **11**) or by the reaction of the chlorophosphine, (Me_3Si)$_2$NP(Cl)[CH($SiMe_3$)CH=CH($SiMe_3$)] (**1**), with organolithium compounds (with MeLi to give **12**, or with *t*-BuLi to give **13**). The new compounds **3** - **13** were fully characterized by multinuclear (^1H, ^{13}C, ^{31}P, and ^{29}Si) NMR spectroscopy and elemental analyses.

Introduction

Recently, there has been considerable interest in the preparative, structural, and coordination chemistry of phosphadienes, the acyclic, conjugated butadiene analogues in which one or more of the carbon atoms are replaced by 2-coordinate phosphorus centers.[2] We have reported, for example, the synthesis[3] and some novel oxidation/cyclization reactions[4] of the 1-phosphadiene **2** which is kinetically stabilized by the steric bulk and π-acceptor properties of the Me_3Si groups along the P=C-C=C backbone. Compound **2** was prepared by dehydrohalogenation of the new chlorophosphine **1** (eq 1) which contained the necessary 1,3-disilylpropenyl substituent on phosphorus.



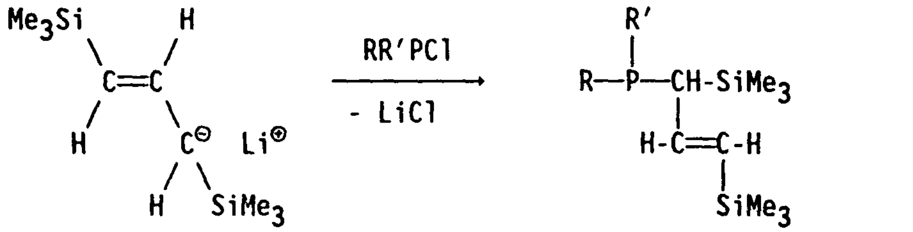
(1)

1 **2**

Because of their potential as precursors to phosphadienes and novel phosphorus heterocycles and as new, multidentate ligands in organometallic systems, we have conducted a more detailed investigation of the chemistry of **1** and related 1,3-disiylypropenylphosphines. Accordingly, we report here the synthesis and NMR structural characterization of a series of new phosphines which contain the 1,3-bis(trimethylsilyl)propenyl substituent. Phosphines. (origin)

Results and Discussion

As reported for the preparation of **1**,[3] the disilylpropenyl group was introduced into the compounds described here by first preparing 1,3-disilylpropenyllithium by treatment of 1,3-disilylpropene with one equivalent of *n*-BuLi and TMEDA (tetramethylethylenediamine) in Et_2O solution. Subsequent addition of one equivalent of simple chlorophosphines afforded the corresponding (1,3-disilylpropenyl)phosphines **3** - **5** (eq 2). Compounds **3** - **5** were obtained in good yields (ca. 60-65%) as colorless, distillable liquids that were fully characterized by ^{1}H, ^{13}C, ^{31}P, and ^{29}Si NMR spectroscopy (Tables I and II) and elemental analyses (Table III).



(2)

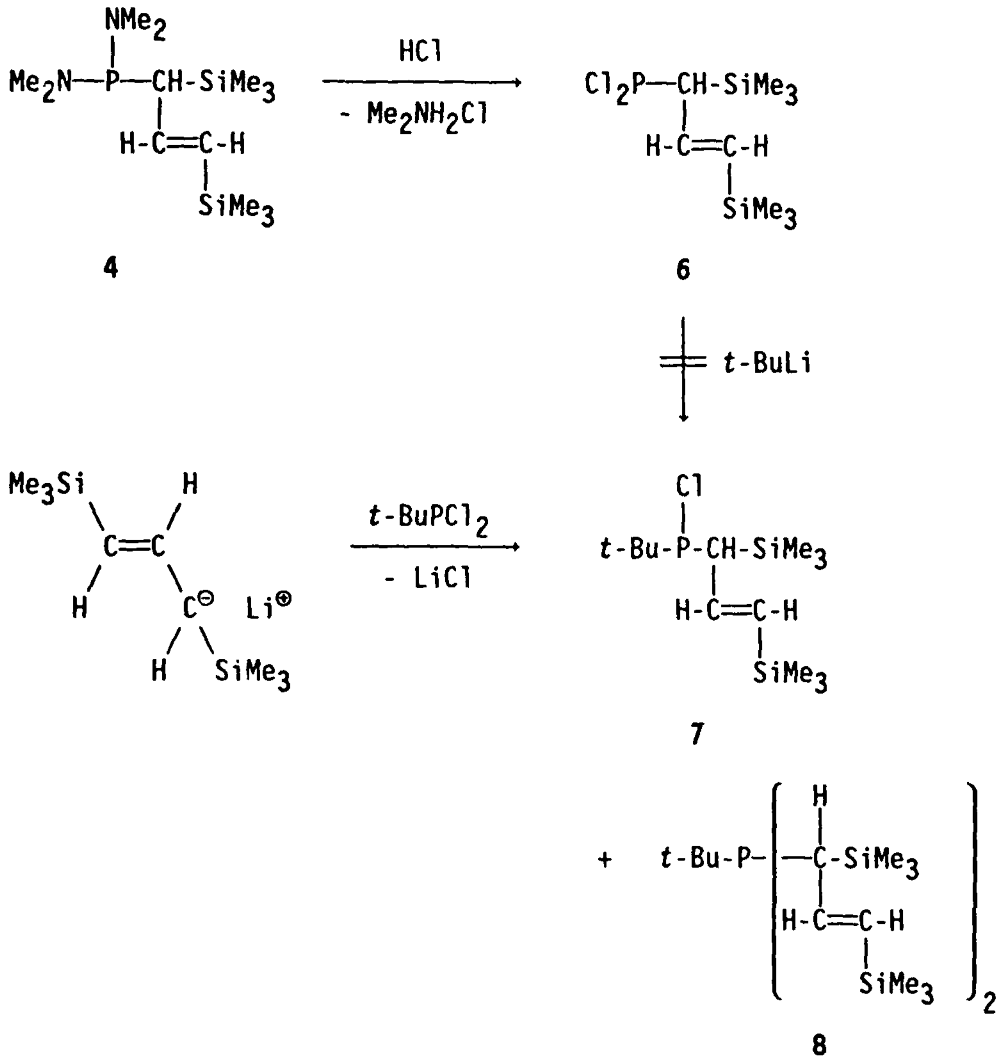
3: R = R′ = Ph

4: R = R′ = NMe_2

5: R = Ph, R′ = NMe_2

The NMR spectroscopic data provide conclusive evidence for the assigned structures of these and the other new compounds prepared in this study. Several features are particularly noteworthy in this regard. First, as expected, the chemical shifts in the ^{31}P NMR spectra are found at ca. 80-90 ppm *upfield* from those of the starting chlorophosphines. Second, in all cases, the vinylic protons must be in a *trans* relationship as indicated by the large (ca. 18 Hz) vinylic $^{3}J_{HH}$ coupling.[5] Third, the α-CH proton gives rise to a doubled doublet pattern in the ^{1}H NMR spectra due to coupling to phosphorus as well as the β-vinylic CH proton. Fourth, two doublets with relatively similar J_{PC} couplings are observed for the vinyl carbons in each compound. The definitive assignment of these two signals was made on the basis of some 2-dimensional ^{1}H/^{13}C chemical shift correlation (HETCOR) experiments. Finally, in the case of **5**, two diastereomers are clearly evident in the ^{31}P NMR spectrum and are confirmed by the existence of *pairs* of signals for many of the ^{1}H, ^{13}C, and ^{29}Si centers. The diastereomers result from the presence of two chiral centers (at phosphorus and the α-carbon) in the molecule.

Compounds such as **4** and **5** that contain P-NMe_2 groups are useful for the synthesis of P-*chloro*phosphines which, in turn, are potential precursors to new 1-phosphadienes analogous to **2**. For example, treatment of the bis(dimethylamino) derivative **4** with an excess of anhydrous HCl (eq 3) results in a downfield shift of the ^{31}P NMR signal from ca. 93 ppm (**4**) to to 194 ppm, indicating the formation of the dichlorophosphine **6**. Although this product could not be purified by distillation due to its thermal instability, the structure of compound **6** was confirmed by ^{1}H and ^{13}C NMR spectral data obtained on the undistilled product which contained less than 5% impurities.

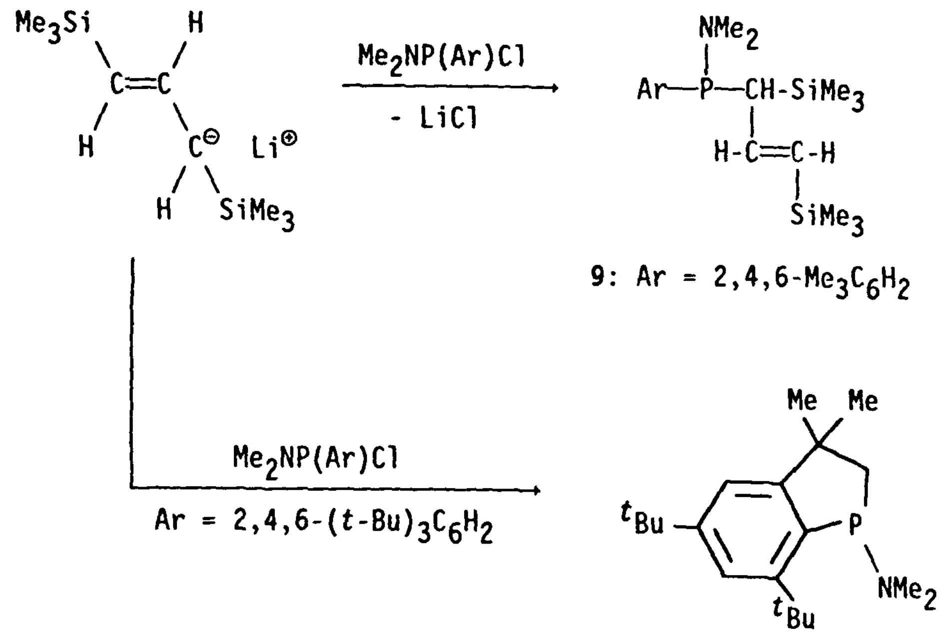


(3)

(4)

An attempt was made to prepare a stable derivative of **6** by treating it with one equivalent of *t*-BuLi. The expected monochlorophosphine **7**, however, was not obtained. The ^{31}P NMR spectrum of the reaction mixture contained four peaks at 25.5, 26.4, 123.1, and 123.8 ppm with the latter two signals being tentatively assigned to the two diastereomers expected for **7**. Upon distillation, extensive decomposition occurred and no products could be conclusively identified. Compound **7**, however, was prepared by a different route. Thus, the reaction of 1,3-disilylpropenyllithium directly with *t*-$BuPCl_2$ (eq 4) afforded **7** in ca. 60% yield as a thermally stable, distillable liquid (Tables I - III). Phosphorus-31, ^{1}H, ^{13}C, and ^{29}Si NMR spectroscopic data indicated that compound **7** was produced as a mixture of two diastereomers in ca. 2 : 1 ratio. This reaction also produced a small amount (ca. 12% yield) of the disubstituted product **8** (eq 4). Fractional distillation resulted in the isolation of **8** in pure form as a second, higher-boiling liquid fraction (Tables I - III).

The synthesis of (disilylpropenyl)phosphines containing other bulky substituents was also of interest in this study. For example, the reaction of 1,3-disilylpropenyllithium with chloro(dimethylamino)-(mesityl)phosphine (eq 5) occurred smoothly to afford the corresponding derivative **9** as a mixture of two diastereomers in ca. 2:3 ratio. Like its P-phenyl analogue **5**, compound **9** was thermally stable to distillation and was fully characterized.



(5)

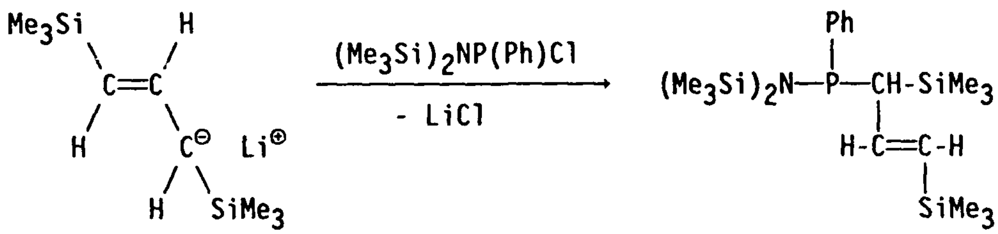
(6)

10

This type of reaction took a very different course when the even more sterically demanding "supermesityl" group, 2,4,6-tri-*tert*-butylphenyl, was employed (eq 6). Thus, treatment of the aryl(chloro)-(dimethylamino)phosphine (prepared *in situ* from Me_2NPCl_2 and the aryllithium reagent[6]) with disilylpropenyllithium did not give the desired substitution product. Instead, cyclization to form **10**, probably as a result of deprotonation of a methyl group on one of the *t*-Bu substituents by the allyl anion, was observed.

The cyclic product **10** was isolated in 32% yield as a crystalline solid. Similar cyclization reactions involving the "super-mesityl" group have been previously reported; however, these reactions were initiated by protic or Lewis acids instead of alkyllithium reagents.[7,8]

In order to further extend the range of known (disilylpropenyl)phosphines, we also prepared three compounds, analogous to **1**, that contain the bis(trimethylsilyl)amino group on phosphorus and other groups in place of the P-chloro substituent. Two different procedures were employed in this phase of the project. As above, the first method involved the reaction of an appropriate chlorophosphine with 1,3-disilylpropenyllithium (eq 7) to afford the P-phenyl derivative **11**. After fractional distillation, **11** was isolated in 77% yield as a single diastereomer (^{31}P NMR δ 40.9) although a small amount (ca. 5 - 10%) of the other isomer was noted in the ^{31}P NMR spectrum of the undistilled product.

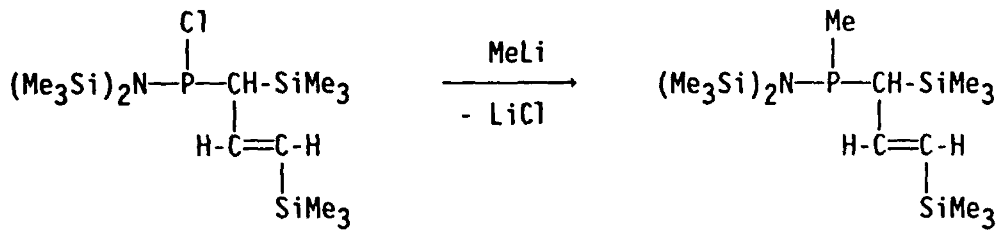


(7)

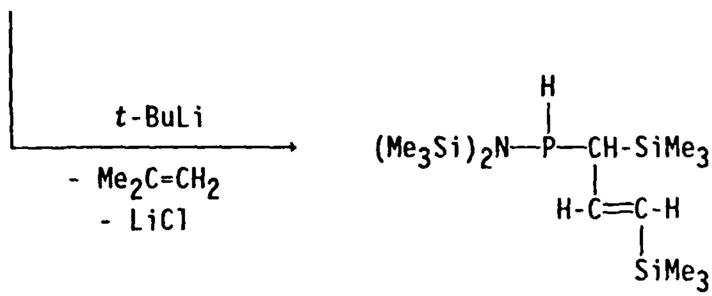
11

In the second approach, the reactivity of the P-Cl bond in **1** toward organolithium reagents was studied. Replacement of the P-Cl group by a P-methyl group was easily achieved using methyllithium (eq 8), thus affording compound **12**. Although the ^{31}P NMR spectrum of the distilled product contained a single peak, the presence of diastereomers of **12** was clearly observed in the ^{1}H and ^{13}C NMR spectra. Two sets of signals were observed for the P-Me and P-CH-Si groups in both the ^{1}H and the ^{13}C NMR spectra and for both of the vinyl carbons in the ^{13}C NMR spectrum (Table I).

Derivatization of the chlorophosphine **1** was also attempted by a reaction with *tert*-butyllithium. In this case, however, simple nucleophilic substitution was not observed. Instead, reduction of the chlorophosphine occurred to give the P-H substituted (allyl)aminophosphine **13** (eq 9). Similar reductions of sterically crowded chlorophosphines by *t*-BuLi, accompanied by evolution of *iso*-butylene, have been observed in other systems.[9] According to the ^{31}P NMR spectrum, compound **13** was formed as two diastereomers in approximately the same ratio as in the chlorophosphine **1**, thus indicating that reduction occurred with the stereochemistry about the phosphorus being maintained. Phosphine **13** was a light yellow liquid that, like most P-H compounds, was reactive toward $CHCl_3$ and CCl_4. All NMR spectra of **13**, therefore, were obtained using benzene-d_6 as the solvent. The ^{31}P NMR chemical shifts are found at -0.4 ppm for the major diastereomer and 7.2 ppm for the minor one. The J_{PH} coupling constants are 209.9 Hz and 206.0 Hz for the major and minor diastereomers, respectively. These values are typical of P^{III}-H moieties.[10]



1 **12** (8)



13 (9)

In summary, this work has shown that it is possible to prepare a wide variety of 3-coordinate phosphines that contain the 1,3-disilylpropenyl substituent. Two complementary synthetic approaches are useful: (1) the reaction of 1,3-disilylpropenyllithium with chlorophosphines (eqs 2, 4, 5, and 7), and (2) the reaction of P-chloro substituted (1,3-disilylpropenyl)phosphines such as **1** with nucleophilic reagents (eqs 8 and 9). Further studies of the chemistry of these new phosphine derivatives are in progress.

Experimental Section

Materials and general procedures. The following reagents were obtained from commercial sources and used without further purification: *n*-BuLi (hexane solution), *t*-BuLi (pentane solution), MeLi (ether solution), Mg metal, bromomesitylene, Me_3SiCl, Me_3SiNMe_2, $(Me_3Si)_2NH$, $CH_2=CHCH_2SiMe_3$, PCl_3, $PhPCl_2$, and Ph_2PCl. Ether, hexane, and TMEDA (tetramethylethylenediamine) were distilled from calcium hydride prior to use. THF was dried by distillation from Na/benzophenone. The (dimethylamino)phosphines, $(Me_2N)_2PCl$, Me_2NPCl_2, and $Ph(Me_2N)PCl$, were prepared by the addition of two or one equivalents of Me_3SiNMe_2 to PCl_3 or $PhPCl_2$, respectively, and were identified by ^{31}P NMR spectroscopy.[11] "Supermesityl" bromide, 2,4,6-(*t*-Bu)$_3C_6H_2Br$, was prepared and converted to the aryllithium derivative according to published procedures.[6] The 1,3-disilylpropene, $Me_3SiCH_2CH=CHSiMe_3$, was prepared in Et_2O/TMEDA solution from $Me_3SiCH_2CH=CH_2$ and *n*-BuLi as described in the literature.[12] 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. The HETCOR 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. Tables I - III summarize the physical, analytical and NMR spectroscopic data.

Preparation of [1,3-Bis(trimethylsilyl)propenyl]lithium. An equimolar mixture of TMEDA (0.5 M in Et_2O) and 1,3-bis(trimethylsilyl)propene (20 - 350 mmol) was cooled to 0°C. One equivalent of *n*-BuLi (2.5 M in hexane) was added and the mixture was stirred for 2 h while warming to room temperature. The solution was then used immediately in the various procedures as described below.

Preparation of $Me_2NP(Ph)[C(H)(SiMe_3)CH=C(H)SiMe_3]$ (5). A 250-mL, 3-necked flask, equipped with a N_2 inlet, septum, addition funnel, and magnetic stirrer, was charged with Et_2O (20 mL) and the chlorophosphine, $Me_2NP(Ph)Cl$ (7.50 g, 40 mmol). The solution was cooled to 0°C, and the disilylpropenyllithium solution (40 mmol, prepared as above) was added slowly from the addition funnel. The mixture was stirred overnight at room temperature and then filtered. Following solvent removal, distillation through a 10 cm column gave **5** as a colorless liquid. Compounds **3** and **4** were prepared from disilylpropenyllithium and Ph_2PCl and $(Me_2N)_2PCl$, respectively, by the same procedure.

Preparation of $Cl_2P[C(H)(SiMe_3)CH=C(H)SiMe_3]$ (6). A 250-mL, 3-necked flask, equipped with a N_2 inlet, septum, magnetic stirrer, and a glass stopper, was charged with hexane (100 mL) and the bis(dimethylamino)phosphine **4** (27 mmol). The solution was cooled to 0°C, and anhydrous HCl gas was bubbled into the mixture via a long syringe needle. When the formation of salt stopped, the HCl gas flow was turned off, and the mixture was stirred for ca. 1 h at room temperature. The mixture was filtered and the solvent was removed under reduced pressure. The crude residue was a colorless liquid, identified as **6** by NMR spectral data (Table I), that quickly turned to a bright yellow color upon heating and, when distillation was attempted, decomposed to a dark amber paste.

Preparation of t-BuP(Cl)[C(H)(SiMe$_3$)CH=C(H)SiMe$_3$] (7). A 1-L, 3-necked flask, equipped with N_2 inlet, magnetic stir bar, addition funnel, and septum, was charged with hexane (250 mL) and PCl_3 (8.7 mL, 100 mmol). The solution was cooled to -78°C and t-BuLi (58.8 mL, 1.7 M, 100 mmol) was added dropwise. After the mixture was stirred for 2 h while warming to room temperature, it was cooled to 0°C and the disilylpropenyllithium solution (100 mmol) was added slowly over a 1.5 h period. The mixture was allowed to slowly warm to room temperature and was stirred overnight. The solution was filtered and the solvent was removed under reduced pressure. Distillation through a short path apparatus, followed by redistillation through a 10-cm column gave **7** and **8** as colorless liquids.

Preparation of $MesP(NMe_2)[C(H)(SiMe_3)CH=C(H)SiMe_3]$ (9). A 500-mL, 3-necked flask, equipped with addition funnel, N_2 inlet, septum, condenser, and magnetic stir bar was charged with THF (75 mL) and Mg metal (2.6 g, 107 mmol). Bromomesitylene (15.3 mL, in 25 mL THF, 100 mmol) was added slowly enough to maintain a steady reflux of the reaction mixture. After this addition, the solution was refluxed for 2 h. The solution was then cooled to -78°C, and Me_2NPCl_2 was added via syringe. The mixture was allowed to warm slowly to room temperature and then refluxed for 1 h. The mixture was cooled to 0°C and the disilylpropenyllithium solution (100 mmol) was added from the addition funnel and the mixture was stirred overnight at room temperature. Most of the solvent was removed under reduced pressure and hexane (200 mL) was added, but the solid residue remained intact. Thus, THF (150 mL) was added to help break up the residue. After settling of the salts, the solution was decanted via canulla and the salts were successively washed two more times with hexane. Following solvent removal, distillation through a 10-cm column gave **9** as a colorless liquid.

Preparation of the Cyclic Derivative 10. A 1-L, 3-necked flask, equipped with condenser, addition funnel, magnetic stir bar, septum, and N_2 inlet, was charged with THF (400 mL) and 2,4,6-tri-*tert*-butylbromobenzene[6a] (28.3 g, 87 mmol). The solution was cooled to -78°C and *n*-BuLi (34.8 mL, 2.5 M, 87 mmol) was added via syringe and the mixture was stirred for 1.5 h at -78°C[6b]. At -78°C, (dimethylamino)dichlorophosphine (12.7 g, 87 mmol) was added and the mixture was stirred while warming to room temperature and was then refluxed for 1 h with stirring. The mixture was cooled to 0°C and the disilylpropenyllithium solution (87 mmol) was added to the mixture via an addition funnel. The mixture was stirred overnight while warming to room temperature. After the solvent was removed under reduced pressure, the residue was dissolved in hexane. The mixture was filtered, and slow evaporation of the hexane afforded **10** as a beige colored solid.

Preparation of $(Me_3Si)_2NP(Ph)[C(H)(SiMe_3)CH{=}C(H)SiMe_3]$ (11). A 1-L, 3-necked flask, equipped with stir bar, septum, N_2 inlet, and addition funnel was charged with Et_2O (150 mL) and $(Me_3Si)_2NH$ (21.0 mL, 100 mmol). The mixture was cooled to 0°C and *n*-BuLi (40.0 mL, 2.5 M, 100 mmol) was added. The mixture was stirred while warming to room temperature for 1.5 h and then was recooled to -78°C. Dichlorophenylphosphine (13.6 mL, 100 mmol) was added and the mixture was stirred for 2 h while warming to room temperature. The disilylpropenyllithium solution (100 mmol) was added from the addition funnel to the mixture at 0°C. The mixture was stirred overnight while at room temperature. After filtration and solvent removal, distillation through a 10-cm column afforded **11** as a very viscous, colorless liquid.

Preparation of $(Me_3Si)_2NP(Me)[C(H)(SiMe_3)CH{=}C(H)SiMe_3]$ (12). A 250-mL, 3-necked flask, equipped with a N_2 inlet, magnetic stirrer, glass stopper, and septum, was charged with Et_2O (100 mL) and the chlorophosphine **1** (18.3 g, 44 mmol). The solution was cooled to 0°C and MeLi (31.7 mL, 1.4 M, 44 mmol) was added via syringe. The mixture was allowed to warm to room temperature and was stirred overnight.

After filtration and solvent removal, distillation through a short-path apparatus gave **12** as a yellow liquid.

Preparation of $(Me_3Si)_2NP(H)[C(H)(SiMe_3)CH{=}C(H)SiMe_3]$ (13). A 250-mL, 3-necked flask, equipped with a N_2 inlet, septum, magnetic stirrer, and glass stopper, was charged with Et_2O (100 mL) and the chlorophosphine **1** (11.8 g, 29 mmol). The solution was cooled to 78°C and *t*-BuLi (15.9 mL, 1.8 M, 29 mmol) was added slowly via syringe. The mixture was allowed to warm slowly and was stirred overnight. After the mixture was filtered and the solvent was removed, distillation through a short-path apparatus and a redistillation through a 10-cm column gave compound **13** as a light yellow liquid.

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Table I. Proton, ^{13}C, and ^{31}P NMR Spectroscopic Data[a]

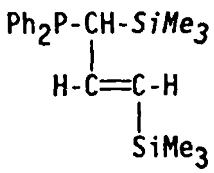
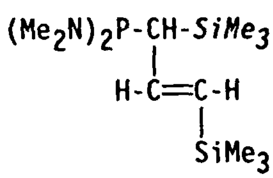
		^1H NMR		^{13}C NMR		^{31}P NMR
Compound	Signal	δ	J_{PH}	δ	J_{PC}	δ
	*Me_3Si*	0.06		-1.35	4.6	-14.6
	Me_3Si	0.02		-0.91		
	PCH	2.84	3.7	37.25	30.6	
3			{10.1}[b]			
	CH=CHSi	6.02	6.4	143.40	5.0	
			{10.1, 18.4}[b]			
	CH=*CH*Si	5.68	3.0	130.53	8.4	
			{18.4}[b]			
	Ph	7.3-7.6[c]		127-139[c]		
	*Me_3Si*	-0.01		-1.54	5.0	92.5
	Me_3Si	0.00		-0.76		
	PCH	2.57	3.6	39.58	21.2	
4			{10.4}[b]			
	NMe_2	2.55	1.5	41.34	4.1	
		2.58	2.4	41.15	4.1	
	CH=CHSi	5.84	7.3	142.93	13.1	
			{10.4, 18.2}[b]			
	CH=*CH*Si	5.43	3.2	128.32	11.1	
			{18.2}[b]			

Table I. Continued.

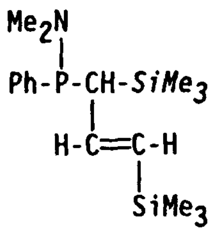
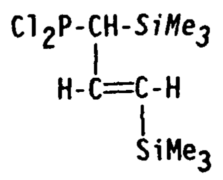
	*Me_3Si*	0.15		-1.28	3.7	59.3
		0.06[d]		-1.47[d]	5.9	55.0[d]
	Me_3Si	-0.07		-0.81		
				-1.06[d]		
5	NMe_2	2.47	9.1	41.98	14.3	
		2.55[d]	9.2	41.56[d]	13.7	
	PCH	2.84	5.8	40.05	34.0	
			{9.8}[b]			
		2.92[d]	0.0	37.56[d]	24.5	
			{10.3, 1.6}[b]			
	CH=CHSi	5.93	8.7	142.95	17.9	
			{9.8, 18.3}[b]			
		6.11[d]	5.9	143.77[d]	5.4	
			{10.3, 18.3}[b]			
	CH=*CH*Si	5.60	3.5	130.64	14.8	
			{18.3, 1.6}[b]			
				129.32[d]	7.6	
	Ph	7.3-7.5[c]		127-140[c]		
	*Me_3Si*	0.08	1.5	-1.50	5.1	191.67
	Me_3Si	-0.01		-1.07		
	PCH	2.46	16.5	52.10	66.2	
6			{9.4}[b]			
	CH=CHSi	5.95	6.2	136.87	5.5	
			{9.4, 18.3}[b]			

Table I. Continued.

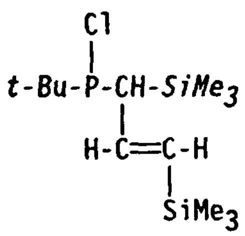
	CH=*CH*Si	5.55	1.5	134.94	5.7	
			{18.[illegible]}[b]			
	*Me*$_3$*Si*	0.61	1.2	-1.47	6.7	127.4
		0.07[d]		-0.25[d]	2.9	126.8[d]
	Me$_3$Si	-0.01		-0.98		
		-0.03[d]		-1.05[d]		
7	*Me*$_3$C	1.07	1.6	26.49	18.2	
		1.03[d]		26.44[d]	15.6	
	PCH	2.02	17.0	40.17	59.9	
			{9.9}[b]			
		2.53[d]	3.6	42.33[d]	53.3	
			{10.6}[b]			
	Me$_3$*C*			36.09	37.4	
				35.74[d]	36.3	
	CH=CHSi	6.17	4.4	142.38		
			{9.9, 18.6}[b]			
		5.85[d]	7.7	142.86[d]	21.7	
			{10.6, 18.4}[b]			
	CH=*CH*Si	5.54	3.6	129.40		
			{18.6}[b]			
		5.38[d]	0.0	131.26[d]	12.8	
			{18.4}[b]			

Table I. Continued.

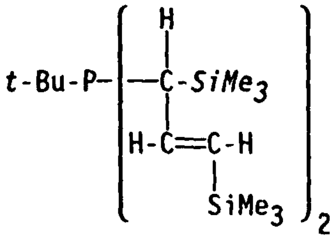
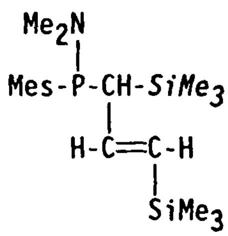
	*Me_3Si*	0.02		-0.21	5.1	3.6
	Me_3Si	-0.02		-0.88		6.2[d]
	Me_3C	1.02	11.6	30.35	13.6	
	Me_3*C*			32.04	24.5	
8	PCH	2.10	3.2	36.94	41.7	
			{11.1}[b]			
	CH=CHSi	5.94	3.2	144.95		
			{11.1, 18.3}[b]			
	CH=*CH*Si	5.32	2.1	129.22	3.8	
			{18.3}[b]			
	*Me_3Si*	0.16		-1.53	5.3	54.6
		0.21[d]	0.7	-1.66[d]	4.0	54.3[d]
	Me_3Si	-0.09		-1.12	0.8	
		-0.10[b]		-0.75[d]	0.7	
9	Me_2N	2.66	9.2	43.06	15.8	
Mes = 2,4,6-$Me_3C_6H_2$		2.63[d]	9.7	43.15[d]	15.1	
	PCH	3.02	1.2	37.58	29.7	
			{10.1}[b]			
		3.48[d]	0.0	40.66[d]	35.1	
			{10.2}[b]			
	CH=CHSi	5.75	5.8	142.13	15.5	
			{18.5}[b]			
		6.23[d]	7.1	145.85[d]	13.4	
			{10.2, 18.4}[b]			
	CH=*CH*Si	5.52	3.0	128.75	12.8	

Table I. Continued.

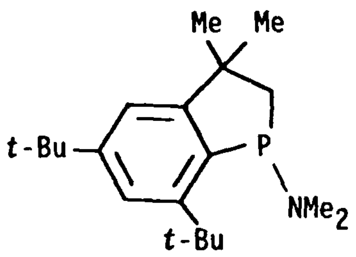
			{18.5}[b]			
		5.73[d]	0.0	128.86[d]	10.9	
			{18.4}[b]			
	2-*Me*-C	2.63		23.66	19.6	
		2.69[d]		24.31[d]	19.8	
	6-*Me*-C	2.72		21.03		
		2.30[d]		21.14[d]		
	3,5-*CH*	6.82		129.76	2.5	
		6.88[d]		130.28[d]	3.4	
	2,6-Me-*C*			143.38, 143.60[d]		
	1-*C*-P			132.81	48.6	
				133.27[d]	30.7	
 10	PCH_2	1.97	16.9	40.27	13.3	73.8
			{11.3}[b]			
		2.04	13.5 {11.3}[b]			
	CMe_2	1.22		31.60		
		1.51		34.82	2.7	
	*C*Me$_2$			45.19	3.0	
	NMe$_2$	2.48	8.2	40.82	13.9	
	P-*C*			134.58	16.3	
	o-C-CMe_3	1.53		31.56	7.2	
	o-C-*C*Me$_3$			37.46	2.5	
	o-*C*			153.04	12.6	
				156.87	9.6	
	m-C-H	7.06	4.0	118.07		

Table I. Continued.

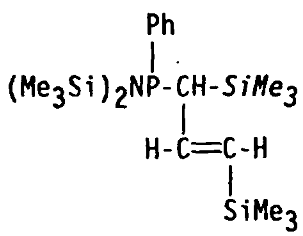
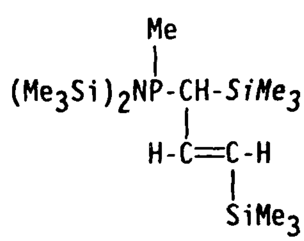
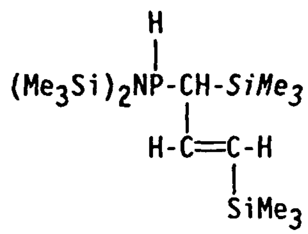
			{1.8}[b]			
		7.36	0.8	122.50	3.3	
			{1.8}[b]			
	p-C-C*Me*$_3$	1.37		31.66		
	p-C-*C*Me$_3$			35.10		
	p-C			152.03		
	*Me*$_3$*Si*	0.13	0.7	-1.48	6.2	40.9
	Me$_3$Si	0.17		-0.49		
	Me$_3$SiN	0.44	1.4	5.18		
		-0.05[e]		4.33[e]	14.2	
11	PCH	2.91	4.9	41.36	44.9	
			{10.6}[b]			
	CH=CHSi	6.15	6.4	144.19	2.6	
			{10.6, 18.4}[b]			
	CH=*CH*Si	5.57	2.6	129.32	7.1	
			{0.8, 18.4}[b]			
	Ph	7.3-7.5[c]		127-145[c]		
	*Me*$_3$*Si*	0.09		-1.01	3.7	39.1
	Me$_3$Si	0.02		-0.75		
	Me$_3$SiN	0.24	1.1	5.18	7.5	
	PMe	1.29	7.4	17.36	27.4	
12		1.37[d]	7.0	19.37[d]	24.0	
	PCH	2.57	4.4	44.30	40.0	

Table I. Continued.

			{10.5}[b]			
		2.43[d]	5.1	46.20[d]	38.9	
			{10.9}[b]			
	CH=CHSi	5.76	7.3	142.76	14.3	
			{10.5, 18.2}[b]			
				145.55[d]	5.8	
	CH=*CH*Si	5.52	3.3	130.60	10.2	
			{18.2}[b]	128.54[d]	8.0	
	*Me_3Si*	0.11	0.7	-2.01	3.9	-0.4
	Me_3Si	0.18		-0.79		7.2[d]
	Me_3SiN	0.29	0.8	3.53	5.2	
	PH	5.50	209.9 {3.6}[b]			
13[f]	PCH	2.70	2.0	44.04	36.8	
			{10.8, 3.6}[b]			
		2.52[d]	1.4			
			{7.0, 2.6}[b]			
	CH=CHSi	6.15	6.4	146.10	14.2	
			{10.5, 18.2}[b]			
	CH=*CH*Si	5.59	3.8	129.78	10.0	
			{18.2}[b]			

[a]Chemical shifts relative to Me_4Si for ^1H and ^{13}C spectra and to H_3PO_4 for ^{31}P spectra; coupling constants in Hz. Solvents: $CDCl_3$ or CH_2Cl_2. [b]J_{HH} values in brackets. [c]Complex multiplet. [d]Resonances due to diastereomers. [e]Hindered rotation about the P-N bond. [f]Benzene solution.

Table II. Silicon-29 NMR Spectroscopic Data[a]

Compound	$PCSiMe_3$ δ	$PCSiMe_3$ J_{PSi}	$=CSiMe_3$ δ	$=CSiMe_3$ J_{PSi}	$NSiMe_3$ δ	$NSiMe_3$ J_{PSi}
3	1.92	15.5	-8.03	1.9		
4	-0.11	19.0	-8.45	2.2		
5	1.26	10.4	-8.05			
	-0.52[b]	21.7	-8.40[b]			
7	1.56	14.4	-9.81	1.1		
	1.43[b]	7.3	-9.51[b]	2.2		
8	-0.71	18.9	-10.17	1.5		
9	1.41	20.5	-8.32	1.4		
	-1.07[b]	21.1	-8.33[b]	5.6		
11	0.52	32.1	-7.76		12.06[c]	9.8
					7.01[c]	24.7

Table II. Continued.

12	-0.40	14.9	-8.33	2.4	6.73	5.9
13	-1.30	14.8	-8.60	2.6	8.61	8.3

[a]Chemical shifts relative to Me_4Si; coupling constants in Hz. Solvent: $CDCl_3$. [b]Diastereomers. [c]Hindered rotation about the P-N bond.

Table III. Preparative and Analytical Data

Compound	Yield %	bp °C/mm Hg	Analysis[a] %C	Analysis[a] %H
3	65	110-135/0.02	67.84	8.22
			(68.06)	(8.43)
4	65	63-67/0.01	51.19	11.18
			(51.44)	(10.62)
5	60	80-87/0.02	60.00	9.47
			(60.48)	(9.55)
7	60	59-65/0.02	50.99	9.98
			(50.54)	(9.79)
8	12	81-107/0.02	57.14	10.93
			(57.57)	(11.20)
9	49	95-130/0.07	63.44	9.85
			(63.46)	(9.83)
10	32	(91-97)[b]	74.87	10.74
			(75.19)	(10.74)

Table III. Continued.

11	77	105-153/0.02	54.86	9.33
			(55.57)	(9.77)
12	71	79-90/0.01	49.05	10.80
			(49.04)	(10.80)
13	33	66-71/0.02	47.99	10.89
			(47.69)	(10.67)

[a]Calculated values in parentheses. [b]Melting point shown in brackets.