proton on the nitrogen, thereby facilitating bond cleavage.[5b]

A second route to cyanoboranes of this type uses a base displacement reaction between $(RO)_2P(O)CH_2NR'_2$ and a cyanoborane adduct. An example would be the utilization of an amine–cyanoborane[7a] or $(CH_3)_2S{\cdot}BH_2CN$[9] as a weak base–cyanoborane adduct reacting with the (aminoalkyl)phosphonate. This process successfully produced the desired cyanoborane (eq 2) in good yield, but production of the donor adduct was time-consuming, and the subsequent product purification was a cumbersome process.

$$PhNH_2{\cdot}BH_2CN + (C_2H_5O)_2P(O)CH_2N(CH_3)_2 \rightarrow (C_2H_5O)_2P(O)CH_2N(CH_3)_2{\cdot}BH_2CN + PhNH_2 \quad (2)$$

In view of the actual and potential usefulness of macrocyclic cyanoborane oligomers, prepared as described above, a more straightforward and convenient procedure for synthesizing $(RO)_2P(O)CH_2NR'_2{\cdot}BH_2CN$ is possible. This procedure affords a simple, less time-consuming method for producing this type of compound in high yield. The cyclic oligomer $(BH_2CN)_x$ reacts with $(RO)_2P(O)CH_2NR'_2$ at room temperature with stirring for 72 h, yielding a product mixture that contains very few contaminants. Heating the reaction mixture leads to decomposition of the starting materials with one decomposition product involving P–C bond cleavage. This results in a lower yield as well as formation of a mixture of products that are difficult to identify. A room-temperature reaction is therefore advantageous and necessary to obtain pure product in higher yield. This temperature dependence of the reaction is in direct contrast to that seen for the amine–cyanoboranes, which are normally refluxed for 3 days.[2] Compounds **1–4** are colorless, oily liquids (Table I); compound **5** is a white crystalline solid.

As noted for amine–cyanoboranes,[2] the C≡N absorption in the IR spectra of $(RO)_2P(O)CH_2NR'_2{\cdot}BH_2CN$ indicates that the cyano and not the isocyano isomer is formed. Characteristic B—H absorptions in the region 2437–2309 cm^{-1} were observed for each compound. A strong NH_2 absorption further distinguished compound **5**. A moderately strong band in the region of 708–674 cm^{-1} is observed for each of these compounds, supporting the presence of a B—N donor/acceptor bond.[10] All the compounds exhibit absorptions in the region 1260–1241 cm^{-1}, which have been assigned to the P=O stretch and are within the range of values observed for the corresponding phosphonates.[5b,11]

The ^1H NMR spectra exhibit features that are consistent with those expected from the structural assignments for the cyanoborane adducts. All of the signals exhibit a downfield shift from the chemical shift values observed in the corresponding phosphonates. As might be expected, the magnitudes of the shifts are largest for those moieties closest to the N–B bond. In compounds **1–4**, the $P–CH_2$ group exhibits a large doublet, indicating the presence of the P–C bond. Compound **5** shows a broad multiplet, which collapses to the characteristic doublet when the N–H resonance is irradiated.

The ^{11}B and ^{31}P NMR data are summarized in Table I for ease of comparison. The ^{11}B NMR spectra for all the compounds show 1:2:1 triplets characteristic of BH_2 moieties. The range of chemical shifts as well as the range of coupling constants is consistent with that of other amine–cyanoboranes and tetracoordinate boron adducts.[12] The ^{31}P NMR data also confirm the formation of the cyanoborane adducts, with the signals showing an upfield shift comparable in magnitude to that observed when the parent phosphonates are compared to their HCl salts.[5b,13]

Acknowledgment. Support of this work by the Utah Agricultural Experiment Station of Utah State University is gratefully acknowledged.

(9) Emri, J.; Gyori, B. *J. Chem. Soc., Chem. Commun.* **1983**, 1303.

(10) Faulks, J. N.; Greenwood, N.; Morris, J. H. *J. Inorg. Nucl. Chem.* **1967**, *29*, 329.
(11) Corbridge, D. E. C. *J. Appl. Chem.* **1956**, *6*, 456.
(12) Heitsch, C. W. *Inorg. Chem.* **1965**, *4*, 1019.
(13) Crutchfield, M. M.; Dungan, C. H.; Van Wazer, J. R. *^{31}P Nuclear Magnetic Resonance*; Topics in Phosphorus Chemistry, Vol. 5; Wiley: New York, 1967; p 9.

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Addition Reactions of a Silylated Iminomethylenephosphorane

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Reactions of the iminomethylenephosphorane $(Me_3Si)_2NP(=NSiMe_3)=CHSiMe_3$ (**2**), a stable three-coordinate P^V species, with some electrophilic and nucleophilic reagents have been studied. Treatment of **2** with various chlorophosphines gave the novel $P^V–C–P^{III}$ systems $(Me_3Si)_2NP(Cl)(=NSiMe_3)CH(SiMe_3)P(X)R$ (**3**, R = X = Ph; **4**, R = X = NMe_2; **5**, R = Ph, X = Cl) via addition across the P=C double bond. The P–Cl derivative **5** readily eliminated Me_3SiCl to afford the cyclic product **6**, an unusual $P^VNP^{III}C$ four-membered-ring system. Compound **2** also underwent rapid addition reactions with both secondary amines and CF_3CH_2OH to yield the four-coordinate aminophosphoranimines $(Me_3Si)_2NP(=NSiMe_3)(CH_2SiMe_3)NR_2$ (**7**, R = Me; **8**, R = Et) and the *P*-(trifluoroethoxy)phosphoranimine $(Me_3Si)_2NP(=NSiMe_3)(CH_2SiMe_3)OCH_2CF_3$ (**9**), respectively. Heating of **9** resulted in elimination of $Me_3SiOCH_2CF_3$ and formation of the P_2N_2 dimer $[Me_3SiNP(=NSiMe_3)CH_2SiMe_3]_2$ (**10**). Addition of methyllithium to **2**, followed by quenching of the intermediate carbanion with either Me_3SiCl or Me_2SiCl_2, gave the highly silylated *P*-methylphosphoranimines $(Me_3Si)_2NP(Me)(=NSiMe_3)CH(SiMe_3)SiMe_2X$ (**11**, X = Me; **12**, X = Cl). When heated, the chlorosilyl derivative **12** readily underwent loss of Me_3SiCl and cyclization to give the novel PNCSi four-membered-ring product **13**. On the basis of these representative reactions, the reactivity of the P=C bond in the iminomethylenephosphorane **2** is contrasted with that in the analogous two-coordinate P^{III} system, the methylenephosphine $(Me_3Si)_2NP=CHSiMe_3$ (**1**).

Introduction

Since the first reports in the 1970s of the synthesis of stable methylenephosphines (A)[1] and iminophosphines (B),[2] the preparative chemistry,[3] reactivity,[4] and coordination chemistry[5] of these two-coordinate P^{III} species have been developed to a considerable

(1) (a) Becker, G. *Z. Anorg. Allg. Chem.* **1976**, *423*, 242. (b) Klebach, Th. C.; Lourens, R.; Bickelhaupt, F. *J. Am. Chem. Soc.* **1978**, *100*, 4887.

(2) Niecke, E.; Flick, W. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 585. (b) Scherer, O. J.; Kuhn, N. *Angew. Chem., Int. Ed. Engl.* **1974**, *13*, 811.

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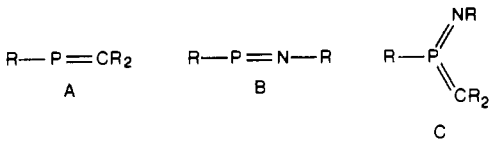
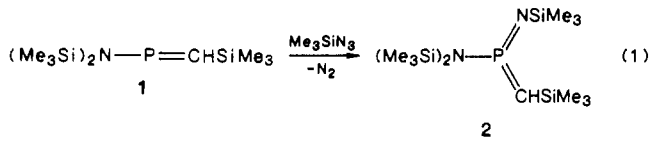
extent. In contrast, the iminomethylenephosphoranes (C),[6] which



A B C

contain both P=C and P=N functionalities in a trigonal-planar P^V arrangement, have received comparatively little attention. Studies of the derivative chemistry of such species should provide synthetically useful information regarding the relative reactivities of (1) a P=C double bond vs a P=N double bond and (2) similarly substituted P=C double bonds in P^{III} (A) and P^V (C) systems.

Recent work in our laboratory has involved the chemistry of the silylated methylenephosphine **1**, which has been shown to undergo a variety of interesting addition, substitution, coordination, and coupling reactions of the P=C moiety.[7-10] The oxidation of **1** with trimethylsilyl azide (eq 1) occurs smoothly to yield the

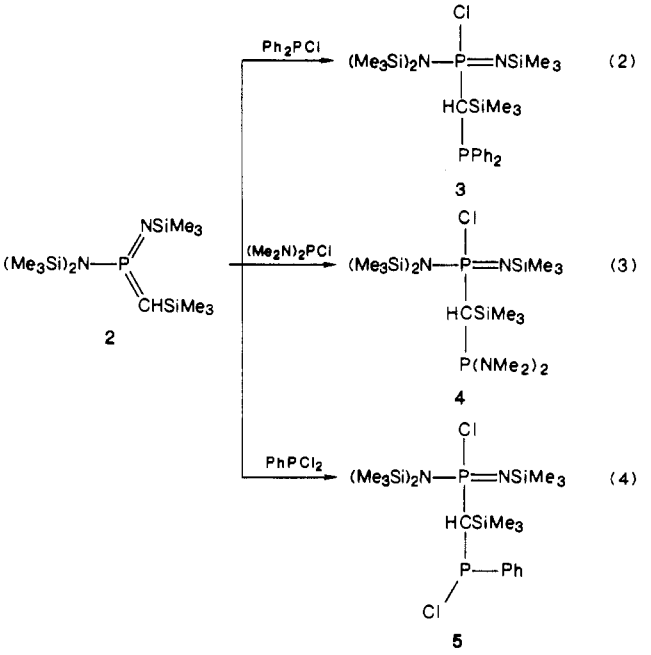


1 2 (1)

iminomethylenephosphorane **2** in high yield as a stable, distillable liquid.[10] As a continuation of these studies of the chemistry of P=C bonds, we report here the reactions of the three-coordinate P^V derivative **2** with selected electrophilic and nucleophilic reagents.

Results and Discussion

In order to compare the reactivity of the iminomethylenephosphorane **2** with the known chemistry of the methylenephosphine **1**, the reactions of **2** with three types of reagents (chlorophosphines, secondary amines, and methyllithium) were studied. A variety of different chlorophosphines reacted smoothly with **2** (eq 2–4) at 0 °C in dichloromethane solution to yield the

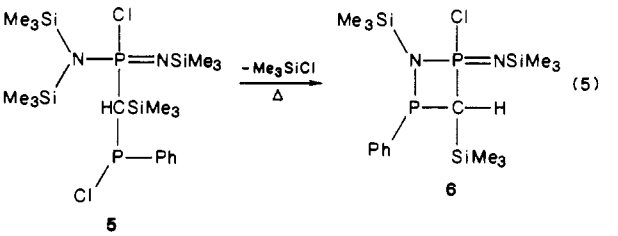


2 3 (2) 4 (3) 5 (4)

P^V–C–P^{III} derivatives **3**–**5** as a result of addition across the P=C bond in **2**.

After solvent removal, compound **3** was obtained as a viscous yellow oil, which gave a satisfactory elemental analysis but underwent extensive decomposition upon attempted distillation. The NMR spectral data (Table I) for the undistilled material is in complete agreement with the proposed structure. In addition to the expected ^1H and ^{13}C NMR signals observed for the Me_3Si and phenyl groups, the central proton of the $CH(SiMe_3)$ group gives rise to two sets of doubled-doublet patterns, consistent with the presence of two chiral centers (CH and P^V) and, hence, diastereomers. The existence of diastereomers for **4** and **5** is also shown by some of the NMR signals (i.e., the NMe_2 proton and carbon resonances of **4** and the ^{31}P peaks of **5**). Compound **4** is considerably more volatile than the PPh_2 analogue **3** and could purified by distillation under reduced pressure without decomposition.

The NMR spectra obtained on the chlorophosphine derivative **5** prior to distillation indicated the presence of a second produt, **6** (ca. 4:1 ratio of **5** to **6**). When the mixture was heated at ca. 100 °C, **5** was completely converted to the cyclic derivative **6** (eq 5) by elimination of Me_3SiCl. Compound **6**, an example of a rare



5 6 (5)

type of P_2NC ring system containing both P^{III} and P^V centers,[11] was isolated by distillation in 72% yield as a clear viscous liquid and was fully characterized by NMR spectroscopy (Table I), elemental analysis, and mass spectroscopy. Confirming evidence of the presence of a P^{III} center in **6** was obtained by its facile reaction with $Fe_2(CO)_9$, which apparently gave the expected $Fe(CO)_4$ complex. Although this complex was thermally unstable and, thus, not well characterized, its ^{31}P NMR spectrum showed the expected[12] downfield shift of the P^{III} signals (see Experimental

(3) See for example: (a) Appel, R.; Knoll, F.; Ruppert, I. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 731. (b) Niecke, E.; Schoeller, 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. (g) Scherer, O. J.; Conrad, H. *Z. Naturforsch.* **1981**, *36B*, 515. (h) Niecke, E.; Rüger, R.; Schoeller, W. W. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 1034. (i) Romanenko, V. D.; Ruban, A. V.; Markovskii, L. N. *J. Chem. Soc., Chem. Commun.* **1983**, 187.

(4) See for example: (a) Appel, R.; Knoch, F.; Zimmerman, 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. (e) Niecke, E.; Wildbredt, D.-A. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 199. (f) Niecke, E.; Flick, W. *Angew. Chem., Int. Ed. Engl.* **1974**, *13*, 134. (g) Paetzold, P.; von Plotho, C.; Niecke, E.; Rüger, R. W. *Chem. Ber.* **1983**, *116*, 1678.

(5) For a review, see: Cowley, A. H.; Norman, N. C. In *Phosphorus-31 NMR Spectroscopy in Stereochemical Analysis*; Verkade, J. G., Quin, L. D., Eds.; Methods in Stereochemical Analysis 8; VCH: Deerfield Beach, FL, 1987; Chapter 17. See also: (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. (f) Scherer, O. J.; Walter, R.; Sheldrick, W. S. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 115. (g) Scherer, O. J.; Kerth, J.; Anselmann, R.; Sheldrick, W. S. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 984.

(6) See for example: (a) Xie, Z.-M.; Neilson, R. H. *Organometallics* **1983**, *2*, 1406. (b) Niecke, E.; Wildbredt, D.-A. *Chem. Ber.* **1980**, *113*, 1549. (c) Niecke, E.; Seyer, A.; Wildbredt, D.-A. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 675.

(7) Li, B.-L.; Neilson, R. H. *Inorg. Chem.* **1986**, *25*, 358.

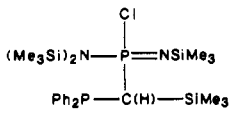
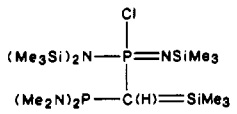
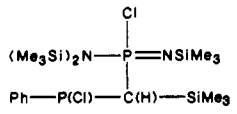
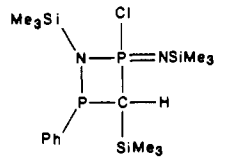
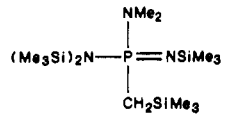
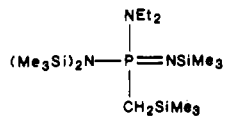
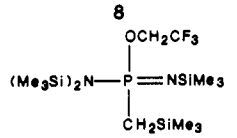
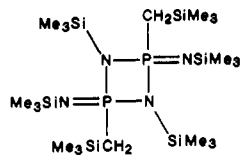
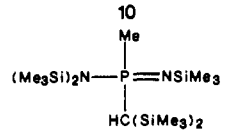
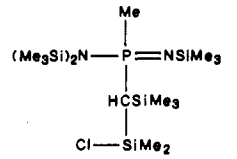
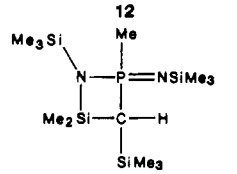
(8) Ford, R. R.; Li, B.-L.; Neilson, R. H.; Thoma, R. J. *Inorg. Chem.* **1985**, *24*, 1993.

(9) Li, B.-L.; Neilson, R. H. *Inorg. Chem.* **1984**, *23*, 3665.

(10) Neilson, R. H. *Inorg. Chem.* **1981**, *20*, 1969.

(11) For a related review, see: Shaw, R. A. *Phosphorus Sulfur* **1978**, *4*, 101.

Table I. Selected NMR Spectroscopic Data[a]

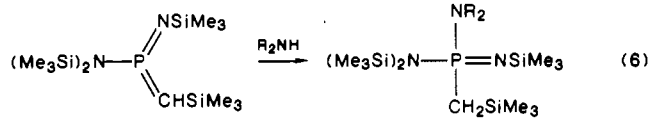
compd	signal	^{1}H NMR δ	^{1}H NMR J_{PH}[b]	^{13}C NMR δ	^{13}C NMR J_{PC}[b]	^{31}P NMR δ[c]
	PCH[d]	2.84	26.4	40.28	39.7	−10.0
			2.9		~0.0	18.6
		3.07	20.5			(151.4)
			4.4			
3						
	PCH	2.18	17.2	39.44	51.7	3.2
			2.5		29.6	70.3
	NCH_3[d,e]	2.55	12.2	39.23	16.7	(24.4)
		2.61	20.0	35.93	4.0	
4						
	CH	2.88	21.5	52.93	42.3	0.2[f]
			2.0		29.2	25.8
						(43.9)
						−1.9[f]
						21.4
5						(25.5)
	CH[d,e]	2.78	23.9	53.30	64.5	−4.9[f]
			4.4		29.2	13.2
		2.92	22.0	53.05	64.4	(43.9)
			3.9		29.2	−2.1[f]
						12.8
6						(24.0)
	NCH_3	2.46	11.1	37.28	3.3	20.1
	PCH_2	1.19	17.6	23.06	102.0	
7						
	PCH_2	1.25	18.2	23.16	105.1	19.1
	NCH_2	2.94[g]		40.72	5.1	
	CH_3	1.10	(7.0)[h]	15.06	5.4	
8						
	PCH_2	1.36	20.5	24.68	109.1	18.9
	OCH_2	3.9–4.3[g]		59.48	3.5	
					(36.1)[i]	
9	CF_3			124.20	12.9	
					(276.5)[i]	
	PCH_2	1.66[d]	20.6	29.42[e]	11.2	−11.9[f]
		1.51	19.6	26.84	14.0	−21.33
10						
	PCH	1.30	21.1	27.89	77.8	18.0
	PMe	1.49	13.1	26.62	68.3	
11						
	PMe	1.46	12.4	25.97	75.1	9.7
	PCH	1.80	13.4	26.76	68.5	
12						
	PMe	1.49	12.2	27.62	77.0	18.0
	PCH	1.41	16.2	26.62	66.2	
13						

[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. Solvent: $CDCl_3$ or CH_2Cl_2. The ^{1}H and ^{13}C NMR spectra of these compounds also exhibited the appropriate resonances for MeSi and Ph moieties as expected. [b] For a given signal, the larger J_{PH} or J_{PC} values are assigned to the P^V center. [c] Upfield δ values assigned to P^V; J_{PP} values in parentheses. [d] Diastereomers observed in ^{1}H spectrum. [e] Diastereomers observed in ^{13}C spectrum. [f] Diastereomers observed in ^{31}P spectrum. [g] Complex multiplet. [h] J_{HH} values in parentheses. [i] J_{FC} values in parentheses.

Section) and the same relative proportion of diastereomers as observed for **6**.

Toward these chlorophosphine reagents, the P=C double bond in the iminomethylenephosphorane **2** is much more reactive than that in the methylenephosphine **1**. In fact, **1** only slowly adds Ph_2PCl to afford a P—C—P derivative[8] and does not react at all with either $(Me_2N)_2PCl$ or $PhPCl_2$. Since $PhPCl_2$ is more electrophilic than Ph_2PCl, this suggests that nucleophilic attack of the chlorophosphine on the highly electrophilic two-coordinate P^{III} center (**1**) is the important mechanistic feature in the case of **1**. On the other hand, in the P^V analogue **2**, the nucleophilic character of the *carbon* end of the more polar $P^{\delta+}=C^{\delta-}$ bond is probably responsible for its higher reactivity toward electrophilic species such as $PhPCl_2$.

An even more striking contrast in the chemistry of these two- and three-coordinate P=C species is found in their reactions with certain protic reagents, especially secondary amines. We have previously reported that **1** reacts with diethylamine in a complex manner that involves not only addition to the P=C bond but also Si—N bond cleavage and other processes, leading eventually to novel P—N—H or N=P—P systems depending on the exact reaction conditions.[7] The reactions of the iminomethylenephosphorane **2** with secondary amines (eq 6), however, are much



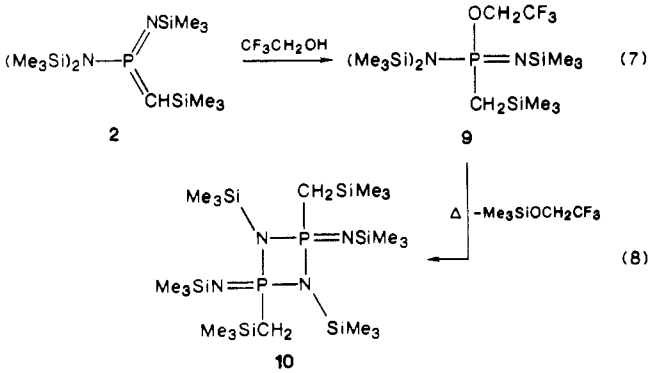
(6)

2

7, R = Me
8, R = Et

more straightforward and involve simple addition to the P=C bond. The new aminophosphoranes **7** and **8** were isolated as colorless liquids and characterized by NMR spectroscopy (Table I) prior to distillation. Both compounds underwent thermal decomposition to unidentified product mixtures upon attempted distillation.

We have also previously reported that methanol reacts with **2** (as it does with **1**) via simple addition to the P=C bond.[10] As part of the present study, compound **2** was treated with 1 equiv of CF_3CH_2OH to yield the *P*-(trifluoroethoxy)phosphoranimine **9** (eq 7) as a stable, distillable liquid. When a neat sample of



(7)

(8)

2 **9** **10**

9 was heated in a sealed glass tube at 190 °C, the P_2N_2 ring system **10** (mixture of cis and trans isomers)[13] was produced in quantitative yield as a result of elimination of $Me_3SiOCH_2CF_3$ (eq 8). The elimination of this silane is also utilized in the synthesis of poly((alkyl/aryl)phosphazenes), $[R_2PN]_n$, from simpler phosphoranimines, $Me_3SiN=P(OCH_2CF_3)R_2$.[14]

The reaction of the iminomethylenephosphorane **2** with a strong nucleophilic reagent, methyllithium, also occurred exclusively via addition to the P=C bond (eq 9). After the intermediate carbanion was quenched with Me_3SiCl, this reaction afforded the

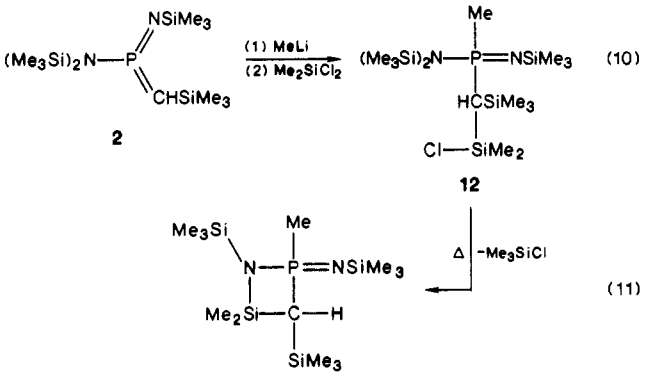
(9)

2 **11**

pentakis(trimethylsilyl)-substituted phosphoranimine **11** as a fully characterized, distillable liquid. Similar reactions of the methylenephosphine **1** with alkyllithium compounds are also much more complicated. For example, when treated with MeLi, **1** undergoes nucleophilic displacment of the $(Me_3Si)_2N$ group from phosphorus and further additions to the P=C moiety to yield a novel P—C—P derivative.[9]

Interestingly, during the distillation of compound **11** at ca. 110 °C under reduced pressure, partial rearrangement to a more symmetrical structural isomer, $(Me_3Si)_2NP(=NSiMe_3)(CH_2SiMe_3)_2$ (**11a**), was observed. The presence of this isomer (as ca. 10–20% of the distillate) was confirmed by the appearance of a second ^{31}P NMR signal (δ 5.9) that was split into a clear quintet ($^2J_{PH}$ = 20.8 Hz) upon proton coupling. The isomeric mixture of **11** and **11a**, although not separable by fractional distillation, gave a satisfactory elemental analysis.

The carbanion generated in the reaction of the iminomethylenephosphorane **2** with MeLi was also treated with 1 equiv of dimethyldichlorosilane (eq 10) to give the unstable chlorosilyl derivative **12**. Attempted distillation of **12** resulted in facile



(10)

(11)

2 **12** **13**

elimination of Me_3SiCl (eq 11) and closure to the novel PNCSi four-membered-ring system **13**. Compound **13** was identified by NMR spectroscopy (Table I) and elemental analysis.

In summary, the important results of this study are (1) that the iminomethylenephosphorane **2** readily undergoes addition of both electrophilic and nucleophilic reagents *selectively to the P=C double bond*, (2) that these reactions are generally more straightforward than they are with the two-coordinate P^{III} analogue **1**, and (3) that the reactions involving difunctional reagents (e.g., $PhPCl_2$ or Me_2SiCl_2) can be useful for the preparation of some unusual small-ring phosphorus compounds.

Experimental Section

Materials and General Procedures. The following reagents were obtained from commercial sources and used without further purification: PCl_3, $PhPCl_2$, Ph_2PCl, Me_2NH, Et_2NH, MeLi, $Fe_2(CO)_9$, Me_3SiCl, Me_2SiCl_2, Me_3SiNMe_2, and CF_3CH_2OH. Bis(dimethylamino)chlorophosphine, $(Me_2N)_2PCl$,[15] was prepared by the addition of 2 molar equiv of Me_3SiNMe_2 to PCl_3 in ether at 0 °C. The iminomethylenephosphorane **2** was prepared according to the published procedure.[10] Ether, pentane, and CH_2Cl_2 were distilled from CaH_2, and THF was distilled from sodium/benzophenone 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. Mass spectra were obtained on a Finnigan GC–MS 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

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(13) For a related $[RP(=NSiMe_3)_2]_2$ dimer, see: Xie, Z.-M.; Neilson, R. H. *Organometallics* **1983**, *2*, 921.
(14) Neilson, R. H.; Wisian-Neilson, P. *Chem. Rev.* **1988**, *88*, 541.
(15) Schmutzler, R. *J. Chem. Soc.* **1965**, 5630.

the synthesis of the new compounds prepared in this study.

Preparation of $(Me_3Si)_2NP(Cl)(=NSiMe_3)CH(SiMe_3)PPh_2$ (3). A 100-mL flask, equipped with a magnetic stirrer, N_2 inlet, and a septum, was charged with the iminomethylenephosphorane **2** (10.0 mmol) and CH_2Cl_2 (30 mL). The solution was cooled to 0 °C, and Ph_2PCl (10.0 mmol) was added slowly via syringe to the stirred mixture. After ca. 30 min, the mixture was allowed to warm to room temperature and was stirred for ca. 1 h. Solvent removal left **3** as a viscous, light yellow liquid that was identified by NMR spectroscopy (Table I). Anal. Calcd: C, 51.29; H, 8.09. Found: C, 51.11; H, 8.03. Attempts to distill **3** under reduced pressure (0.01 mm) led to extensive decomposition.

Preparation of $(Me_3Si)_2NP(Cl)(=NSiMe_3)CH(SiMe_3)P(NMe_2)_2$ (4). In a similar fashion, compound **2** (20.0 mmol) was treated with an equimolar amount of $(Me_2N)_2PCl$ to afford **4** as a distillable, colorless liquid (74% yield; bp 96 °C (0.01 mm)). Anal. Calcd: C, 39.31; H, 9.95. Found: C, 39.81; H, 9.60.

Preparation of $(Me_3Si)_2NP(Cl)(=NSiMe_3)CH(SiMe_3)P(Cl)Ph$ (5) and the Cyclic Derivative 6. By the same procedure, $PhPCl_2$ (10.0 mmol) was added to a stirred solution of **2** (10.0 mmol) in CH_2Cl_2 (30 mL). After the mixture was allowed to warm to room temperature, the solvent was removed under reduced pressure. Analysis of the crude yellow liquid by NMR spectroscopy (Table I) showed that a mixture of **5** and **6** was present. This mixture was then heated at 100 °C for ca. 1 h, and Me_3SiCl was removed under reduced pressure and identified by its ^1H NMR spectrum. From the orange residue, **6** was isolated by fractional distillation as a colorless liquid (72% yield; bp 106–110 °C (0.01 mm)). Anal. Calcd: C, 44.16; H, 7.71. Found: C, 44.01; H, 7.86. The mass spectrum of **6** showed a molecular ion (M^+) at m/e 434 and a base peak at m/e 419 ($M^+ - CH_3$).

Reaction of 2 with $Fe(CO)_4$. Compound **2** (2.0 mmol) was added via syringe to a stirred suspension of $Fe_2(CO)_9$ (2.0 mmol) in pentane (25 mL), and the mixture was stirred overnight at room temperature. Solvent removal left a very viscous red oil that was characterized by ^{31}P NMR spectroscopy (diastereomers: δ −22.8, 111.7 (J_{PP} = 41.5 Hz); δ −12.8, 101.8 (J_{PP} = 34.2 Hz)). This $Fe(CO)_4$ complex of **2** was too thermally unstable for elemental analysis, and it resisted all attempts at recrystallization.

Preparation of $(Me_3Si)_2NP(=NSiMe_3)(CH_2SiMe_3)NR_2$ (7, R = Me; 8, R = Et). In a typical experiment, Et_2NH (20.0 mmol) was added via syringe to a stirred solution of **2** (20.0 mmol) in CH_2Cl_2 at 0 °C. The mixture was allowed to warm to room temperature and was stirred for 1 h. Solvent removal gave **8** as a pale yellow liquid, which was easily characterized by NMR spectroscopy (Table I). Attempts to distill the product under reduced pressure (0.01 mm), however, resulted in decomposition to unidentified products (with several ^{31}P NMR signals in the range of δ −10 to −25). The Me_2N analogue **7** was prepared by a similar procedure except that the amine, measured as a liquid at −78 °C, was allowed to bubble slowly into the solution of **2**. The product **7** was similarly unstable to distillation, but a satisfactory elemental analysis was obtained on a sample prior to distillation. Anal. Calcd: C, 43.96; H, 10.82. Found: C, 43.67; H, 10.81.

Preparation of $(Me_3Si)_2NP(=NSiMe_3)(OCH_2CF_3)CH_2SiMe_3$ (9). A 250-mL flask, equipped with a magnetic stirring bar, N_2 inlet, and a septum, was charged with Et_2O (40 mL) and **2** (20.0 mmol). This solution was cooled to 0 °C, and an equimolar amount of CF_3CH_2OH was added slowly via syringe. The reaction mixture was allowed to warm to room temperature. Solvent removal left a white waxlike solid. Distillation gave **9** as a colorless liquid (80% yield; bp 86 °C (0.1 mm)), which crystallized on standing at room temperature. Anal. Calcd: C, 38.76; H, 8.67. Found: C, 38.48; H, 8.44.

Preparation of $[Me_3SiNP(=NSiMe_3)CH_2SiMe_3]_2$ (10). A neat sample of freshly distilled **9** (10.0 mmol) was sealed under vacuum in a heavy-walled glass ampule. The ampule was heated at 190 °C for 3 days in a thermoregulated oven, during which time the sample changed from colorless to light brown. The $Me_3SiOCH_2CF_3$ byproduct (98% yield) was removed under vacuum and identified by ^1H NMR spectroscopy. The solid residue, which could be recrystallized from cold hexane, was subsequently identified as the dimer **10**. Anal. Calcd: C, 41.05; H, 9.99. Found: C, 40.78; H, 9.94.

Preparation of $(Me_3Si)_2NP(Me)(=NSiMe_3)CH(SiMe_3)_2$ (11). A 250-mL flask, equippd with a magnetic stirring bar, N_2 inlet, and a septum, was charged with the iminomethylenephosphorane **2** (16.0 mmol) and THF (30 mL). The mixture was cooled to −78 °C, and MeLi (16.0 mmol, 1.4 M in Et_2O) was added via syringe. After the mixture was stirred for 1 h at −78 °C, an equimolar amount of Me_3SiCl was added and the mixture was allowed to warm slowly to room temperature. Hexane (ca. 30 mL) was added, and the white solid (LiCl) was allowed to settle. The supernatant solution was decanted from the solid, and the solvents were removed under reduced pressure. Disillation afforded **11** as a colorless liquid (61% yield; bp 108–110 °C). Anal. Calcd: C, 45.08; H, 10.90. Found: C, 44.99; H, 10.55. A small amount (ca. 10%) of the structural isomer **11a** was observed by ^{31}P NMR spectroscopy in the distilled product (see text).

Preparation of $(Me_3Si)_2NP(=NSiMe_3)(Me)(CHSiMe_3)SiMe_2Cl$ (12) and the Cyclic Derivative 13. A 250-mL flask, equipped with a magnetic stirring bar, N_2 inlet, and a septum, was charged with THF (40 mL) and **2** (16.0 mmol). After this mixture was cooled to −78 °C, MeLi (16.0 mmol, 1.4 M in Et_2O) was added slowly via syringe. The solution of the resulting anion was stirred at −78 °C for 30 min. Dimethyldichlorosilane (16.0 mmol) was added via syringe, and the reaction mixture was allowed to warm to room temperature. Isolation of the product as described above for **11** left a colorless residue that, by NMR spectroscopic analysis (Table I), was identified as compound **12**. Attempts to distill **12** led to elimination of Me_3SiCl to afford the cyclic derivative **13** as a colorless liquid (61% yield; bp 108–110 °C (0.04 mm)). Anal. Calcd: C, 45.06; H, 10.92. Found: C, 44.87; H, 10.55.

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

Registry No. **2**, 76946-93-5; (*R**,*R**)-**3**, 118831-07-5; (*R**,*S**)-**3**, 118798-38-2; (*R**,*R**)-**4**, 118798-39-3; (*R**,*S**)-**4**, 118798-40-6; (*R**,*R**)-**5**, 118798-41-7; (*R**,*S**)-**5**, 118798-42-8; *cis*-**6**, 118798-43-9; *trans*-**6**, 118798-44-0; **7**, 118798-45-1; **8**, 118798-46-2; **9**, 118798-47-3; **10**, 118798-48-4; **11**, 118798-49-5; **11a**, 118798-52-0; **12**, 118798-50-8; **13**, 118798-51-9; Ph_2PCl, 1079-66-9; $(Me_2N)_2PCl$, 3348-44-5; $PhPCl_2$, 644-97-3; $Fe_2(CO)_9$, 15321-51-4; Et_2NH, 109-89-7; $Me_3SiOCH_2CF_3$, 56859-55-3; dimethyldichlorosilane, 75-78-5.