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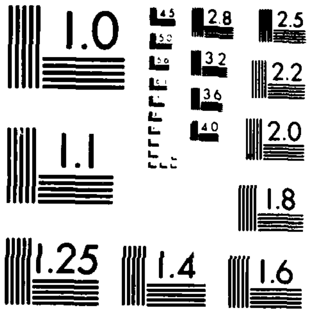

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Mesityl-Phosphorus Compounds: Synthesis of a New Imino(Methylene)phosphorane and Its Dimers

by

Ze-min Xie and Robert H. Neilson

Prepared for Publication

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Organometallics

Texas Christian University
Dept. of Chemistry
Fort Worth, TX 76129

May 25, 1983

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(Silylamino)phosphine	Iminophosphorane
phosphine	methylene phosphorane
phosphinimine	imino(methylene)phosphorane

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

The reaction of CCl_4 with the sterically congested (silylamino)phosphine $(Me_3Si)_2NP(R)CH_2SiMe_3$ (1, R = 2,4,6-$Me_3C_6H_2$) unexpectedly yields the 4-membered P_2N_2 ring system $[Me_3SiCH{=}P(R){-}NSiMe_3]_2$ (2). Heating of the dimer 2 under a dynamic vacuum results in distillation of the monomeric, 3-coordinate

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double bond

imino(methylene)phosphorane R-P(=$CHSiMe_3$)(=$NSiMe_3$) (3). Compound 3 exhibits reasonable stability at room temperature but reverts to the dimer 2 on standing for a few days. Treatment of 3 with methanol affords the stable addition product $Me_3SiN{=}P(R)(OMe)CH_2SiMe_3$ (4). Direct bromination of the phosphine 1 occurs to give the expected P-bromophosphinimine 5 which, by reaction with $LiOCH_2CF_3$, is converted to $Me_3SiN{=}P(R)(OCH_2CF_3)CH_2SiMe_3$ (6). When either the dimer 2 or the monomer 3 is heated in a sealed tube, an isomeric, 4-membered PCPN dimer 7 is obtained quantitatively. Proton, ^{13}C, and ^{31}P NMR data are reported for the new compounds and the CCl_4 reaction of 1 is contrasted to that observed for related systems.

Contribution from the
Department of Chemistry
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Mesityl-Phosphorus Compounds: Synthesis of a New Imino(methylene)phosphorane and Its Dimers[1]

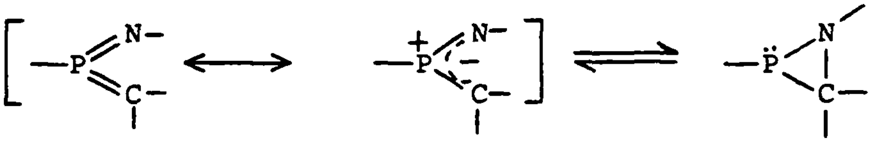
ZE-MIN XIE and ROBERT H. NEILSON*

Abstract

The reaction of CCl_4 with the sterically congested (silylamino)phosphine $(Me_3Si)_2NP(R)CH_2SiMe_3$ (**1**, R = 2,4,6-$Me_3C_6H_2$) unexpectedly yields the 4-membered P_2N_2 ring system $[Me_3SiCH{=}\underset{|}{P}(R){-}\underset{|}{N}SiMe_3]_2$ (**2**). Heating of the dimer **2** under a dynamic vacuum results in distillation of the monomeric, 3-coordinate imino(methylene)phosphorane $R{-}P({=}CHSiMe_3)({=}NSiMe_3)$ (**3**). Compound **3** exhibits reasonable stability at room temperature but reverts to the dimer **2** on standing for a few days. Treatment of **3** with methanol affords the stable addition product $Me_3SiN{=}P(R)(OMe)CH_2SiMe_3$ (**4**). Direct bromination of the phosphine **1** occurs to give the expected P-bromophosphinimine **5** which, by reaction with $LiOCH_2CF_3$, is converted to $Me_3SiN{=}P(R)(OCH_2CF_3)CH_2SiMe_3$ (**6**). When either the dimer **2** or the monomer **3** is heated in a sealed tube, an isomeric, 4-membered PCPN dimer **7** is obtained quantitatively. Proton, ^{13}C, and ^{31}P NMR data are reported for the new compounds and the CCl_4 reaction of **1** is contrasted to that observed for related systems.

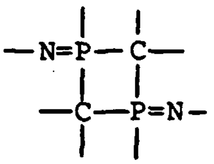
Introduction

Several recent studies have dealt with the synthesis, structure, and reactivity of a novel class of 3-coordinate phosphorus-V compounds known as imino(methylene)phosphoranes (A). By variation of the steric and electronic properties of the substituent groups, such systems have been obtained as kinetically stabilized monomers (A)$^{2-5}$, as dimers of two types (C^{3} and D^{3,4}), and, in one case, as the isomeric 3-membered PNC ring (B)^{4}. Unsymmetrical dimers of type E, however, have not been observed. Moreover, all of these compounds reported to date have contained bulky dialkyl or disilylamino substituents on phosphorus.



A

B



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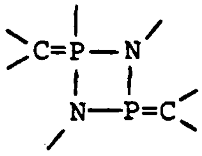
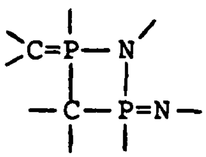
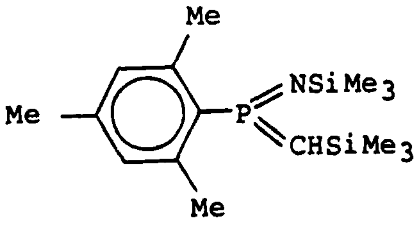


D



E

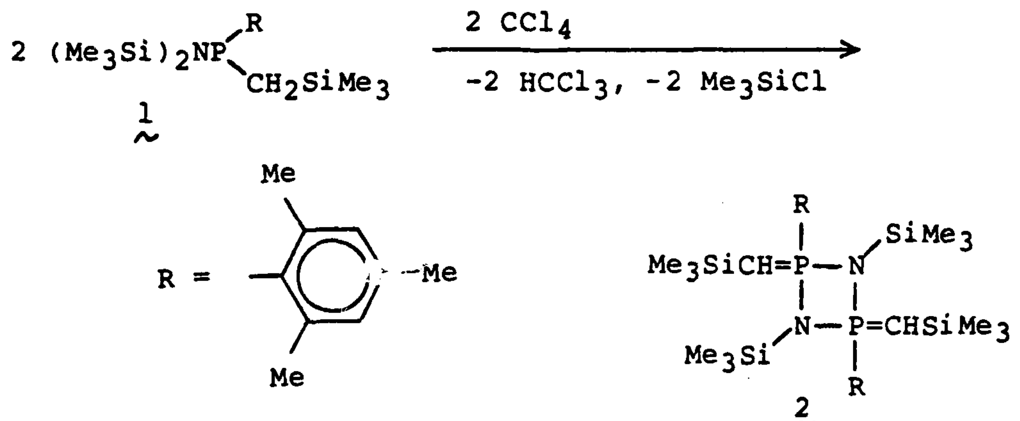
As part of our current investigation^{5} of the chemistry of P-mesityl substituted compounds, we report here the synthesis of a new imino(methylene)phosphorane. This compound exhibits



limited thermal stability at room temperature as a monomer which, depending on temperature, forms either the P_2N_2 (**D**) or the novel PCPN (**E**) dimers.

Results and Discussion

The new compounds described herein were obtained as derivatives of the recently prepared[6] P-mesityl substituted (silylamino)phosphine **1**. When phosphine **1** was treated with an excess of carbon tetrachloride (eq 1) at 0°C in the absence of solvent, the novel four-membered P_2N_2 ring product **2** was isolated in about 70% yield. The characterization and possible formation pathway of compound **2** are discussed below.

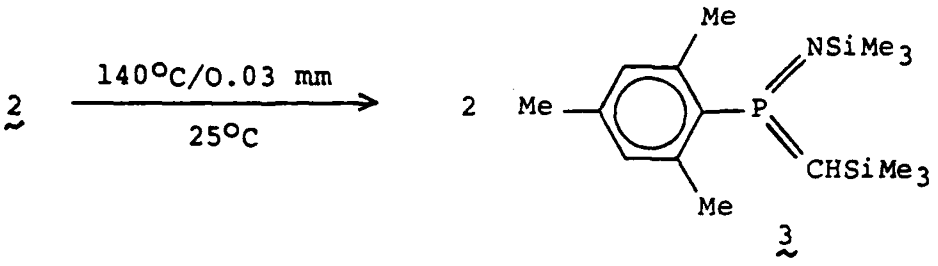


1

2

(1)

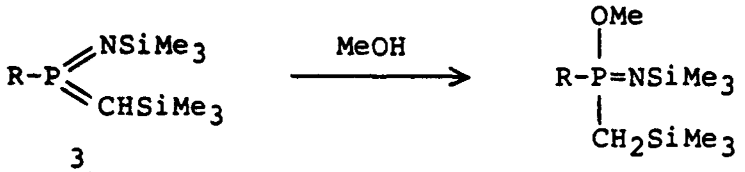
The crystalline solid **2** (mp 145°C) was recognized as being one possible dimeric form of the 3-coordinate phosphorus-V compound, mesityl(trimethylsilylimino)(trimethylsilylmethylene) phosphorane (**3**). Indeed, we initially assumed that **2** was formed via the intermediacy of the thermally unstable monomer **3**. This hypothesis was subsequently rejected upon finding that the thermolysis of **2** (eg 2) gave the monomer **3** as an isolable, reasonably stable compound. Thus, when the dimer **2** was heated



(2)

slightly below its melting point in a vacuum distillation apparatus, a colorless liquid distillate (bp 91-93°C/0.03mm) was collected in high yield. The liquid was shown by NMR spectroscopy to be a mixture consisting largely of the monomer **3** with lesser amounts of the dimer **2**. On standing overnight, crystallization of the dimer occurred, leaving **3** as the spectroscopically pure supernatant liquid. After several days at room temperature, complete conversion of **3** to the crystalline dimer was observed.

Due to its limited thermal stability, the 3-coordinate phosphorane **3** was not submitted for standard elemental analysis. Satisfactory analytical data were obtained, however, for the dimer **2**, an isomeric PCPN compound (see below), and the MeOH addition product **4** (eq 3). In addition to the formation of these stable derivatives, the identity of **3** is confirmed by NMR spectroscopy (Table I). The ^{31}P chemical shift of +122 ppm and the chemical shifts (^{1}H and ^{13}C) and ^{31}P coupling constants of the P=CH moiety are in good agreement with data reported on other imino(methylene)phosphoranes$^{2-5}$. Like the related compound $(Me_3Si)_2N\text{-}P(=CHSiMe_3)(=NSiMe_3)^5$, the reaction of **3** with one equivalent of MeOH (eq 3) occurs smoothly to afford the P-methoxyphosphinimine **4** as a distillable, fully-characterized derivative.



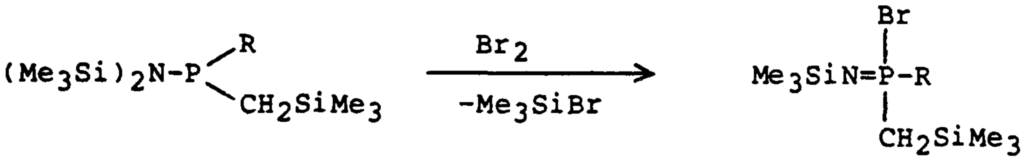
$$\text{R-P}(=\text{NSiMe}_3)(=\text{CHSiMe}_3) \xrightarrow{\text{MeOH}} \text{R-P}(\text{OMe})(\text{CH}_2\text{SiMe}_3)=\text{NSiMe}_3 \qquad (3)$$

3

R = mesityl

4

A compound analogous to 4, containing the trifluoroethoxy group instead of methoxy, was prepared by a different procedure as part of this study. Direct bromination (eq 4) of the starting phosphine 1 proceeds as expected with elimination of Me_3SiBr to yield the P-bromophosphinimine 5. Subsequent reaction with lithium trifluoroethoxide (eq 5) affords the more thermally stable product 6. Phosphinimines 5 and 6 are of interest as possible precursors to cyclic[7] or polymeric[8] phosphazenes which can result from loss of Me_3SiX ($X = Br, OCH_2CF_3$). More to the point of this paper is the finding that the bromo compound 5 decomposes to some extent via elimination of HBr. When a freshly

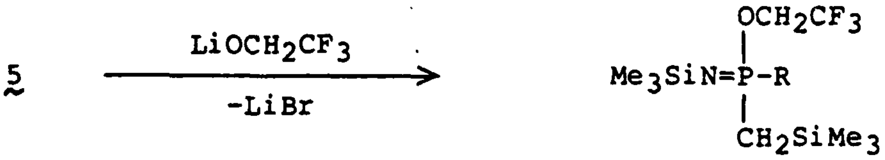


$$(\text{Me}_3\text{Si})_2\text{N-P}(\text{R})(\text{CH}_2\text{SiMe}_3) \xrightarrow[-\text{Me}_3\text{SiBr}]{\text{Br}_2} \text{Me}_3\text{SiN=P}(\text{Br})(\text{CH}_2\text{SiMe}_3)\text{-R} \qquad (4)$$

1

5

R = mesityl

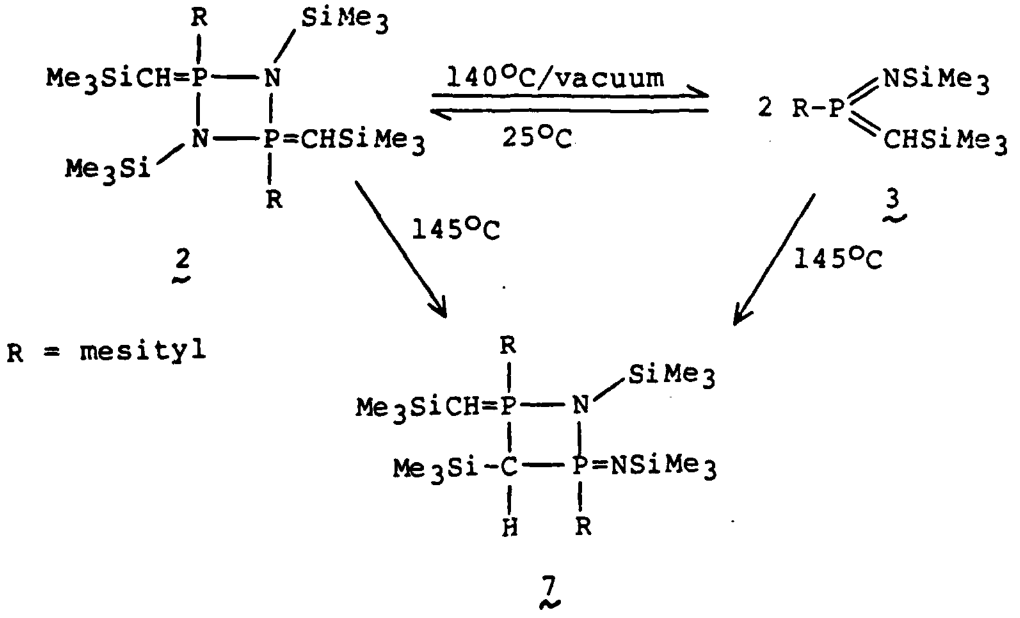


$$5 \xrightarrow[-\text{LiBr}]{\text{LiOCH}_2\text{CF}_3} \text{Me}_3\text{SiN=P}(\text{OCH}_2\text{CF}_3)(\text{CH}_2\text{SiMe}_3)\text{-R} \qquad (5)$$

6

prepared and spectroscopically pure sample of 5 is distilled, the distillate is shown by NMR to contain substantial amounts of the HBr-elimination product 3 and its dimer 2. Unfortunately, more vigorous heating (sealed tube, 160°C, 2 h), gives a complex mixture resulting from loss of Me_3SiBr as well as HBr. The possibility of base-assisted dehydrohalogenation of halophosphinimines such as 5 is under current investigation.

As mentioned above, the 3-coordinate phosphorane 3 dimerizes across the P=N bond to yield 2 (eq 2) at room temperature. Other experiments, however, show that 2 is not the thermodynamically most stable dimer of 3. Thus, if neat samples of either 2 or 3 are heated in a sealed, evacuated tube at 145°C (i.e., just above the melting point of 2) for several hours, then rearrangement (eq 6) to the novel PCPN four-membered ring system 7 occurs quantitatively. The unsymmetrical dimer 7 (mp 158-

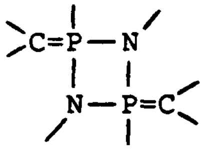


R = mesityl

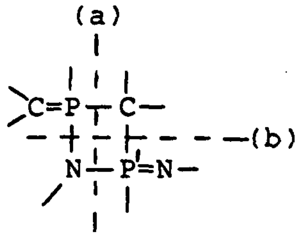
(6)

160°C) simply sublimes when it is heated under a dynamic vacuum. The monomer 3, therefore, is not produced by the thermal cracking of 7 as it is from the symmetrical dimer 2.

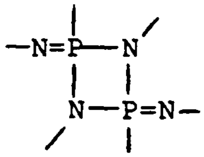
In addition to satisfactory elemental analyses and molecular weight determinations (by mass spectroscopy and cryscopically in benzene), the ^{31}P NMR spectra provide good structural evidence for dimers 2 and 7. Most importantly, the ^{31}P spectrum of the unsymmetrical dimer 7 consists of 2 doublets at +10.9 and -10.6 ppm with $^{2}J_{PP}$ = 15.5 Hz, consistent with 2 nonequivalent phosphorus atoms within the same molecule. Moreover, there is a smooth and internally consistent trend in the ^{31}P shifts of compounds 2, 7, and the bis(imino)phosphorane dimer 8 which we have recently reported[6]. For example, the average of the two ^{31}P shifts of 7 is almost exactly equal to the average of the values for the symmetrical model compounds 2 and 8.



2: δ_P , +22.3



7: δ_P , +10.9
$\delta_{P'}$, -10.6



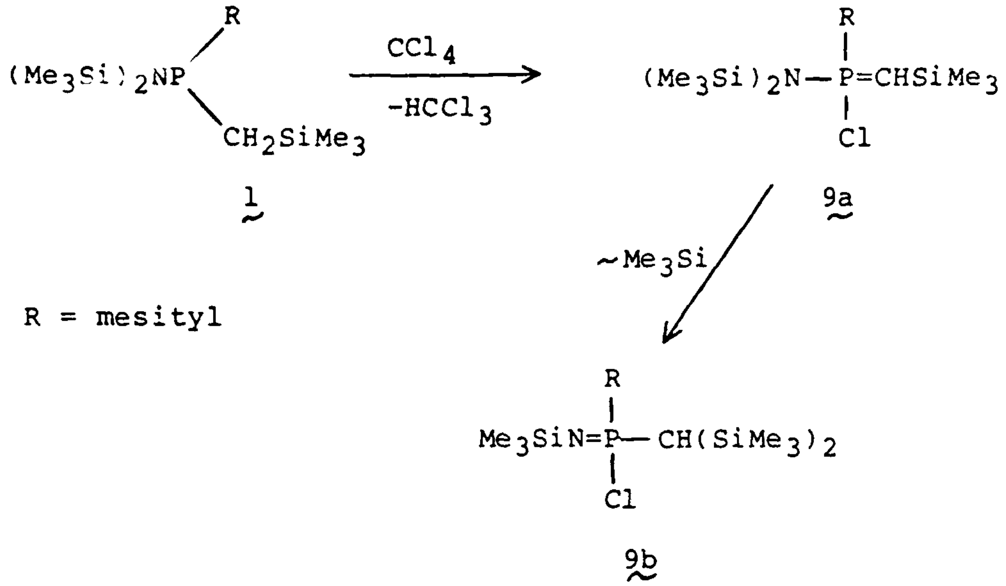
8: δ_P , -19.7(cis)
-24.7(trans)

The mass spectral fragmentation patterns of dimers 2 and 7 are also in accord with the proposed structures. For example, the spectrum of 2 contains significant peaks for the dimer and monomer at *m/e* 646 and 323, respectively. Of more significance is the fact that 7 gives both a parent ion peak of m/e 646 and a set of 3 peaks (m/e 324, 323, 322) corresponding to the 3 possible monomer fragments which could result from symmetrical (a) or unsymmetrical (b) cleavage of the dimer 7.

The proton and ^{13}C NMR spectral data (Table I) provide additional evidence for the structures of these dimers. Some relevant points include: (1) the multiplicity of Me_3Si peaks in the ^1H NMR spectra (2 signals for 2, and 4 signals for 7), (2) the relatively high-field resonance[9] observed for the ylide proton (P=CH, δ 0.60, J_{PH} = 19.8 Hz) of 2; the corresponding signal of 7 is partially obscured by a Me_3Si peak, and (3) the coupling to two phosphorus atoms observed for the CH moiety (both ^1H and ^{13}C) in the PCPN ring of 7.

The formation of the dimer 2 in high yield from the CCl_4 reaction of phosphine 1 is, indeed, an unexpected result. Especially perplexing is the fact that the monomer 3 is not observable when the reaction is monitored by ^1H and ^{31}P NMR spectroscopy. When prepared by thermal cracking of the dimer 2, however, compound 3 exhibits long-term stability in solution at room temperature. Therefore, the intermediacy of 3 in the CCl_4 reaction, which is rapid at 0°C, seems to be precluded.

Based on other recent work,[10,11] the reaction of 1 with CCl_4 was expected to proceed with elimination of $HCCl_3$ and silyl migration from nitrogen to carbon to yield phosphinimine 9b (eq 7), probably via the ylide intermediate 9a. This pathway seemed



(7)

quite reasonable since it has been observed for a large series of similar reactions involving (silylamino)phosphines containing the CH_2SiMe_3 group[11]. The 1,2-elimination of Me_3SiCl from either **9a** or **9b** could then yield the imino(methylene)phosphorane **3**. However, since **3** is not observed in the reaction mixture, the formation of dimer **2** must occur by a more complicated, probably bimolecular, pathway. Efforts are underway to synthesize **9b** and related compounds by other preparative methods in order to further address this problem.

Experimental Section

Materials and General Procedures. The following reagents were obtained from commercial sources and used without purification: Br_2, *n*-BuLi, CCl_4, CF_3CH_2OH, and MeOH. Benzene, CH_2Cl_2, Et_2O, and hexane were distilled from CaH_2 prior to use.

The starting phosphine $(Me_3Si)_2NP(mesityl)CH_2SiMe_3$ (1) was prepared by a straightforward procedure as described elsewhere[6]. Proton NMR spectra were recorded on a Varian EM-390 spectrometer; ^{13}C and ^{31}P NMR, both with ^1H decoupling, were obtained in the FT mode on a JEOL FX-60 instrument. Mass spectral data were obtained on a Finnagin GC-MS system. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, N.Y. All reactions and other manipulations were carried out under an atmosphere of dry nitrogen or under vacuum. The procedures described herein are typical of those used for the preparation of the new compounds in this study.

P_2N_2 Dimer, 2. Carbon tetrachloride (20 mL, 0.20 mol) was added at 0°C with stirring to a neat sample of phosphine 1[6] (41.0 g, 0.103 mol). After stirring for 6 hours at 0°C, the mixture was warmed to room temperature and the excess CCl_4 and other volatiles were removed under vacuum. Chloroform, Me_3SiCl, and a small amount of Me_3SiCCl_3 were identified in the volatile mixture by ^1H NMR. The remaining solid was dissolved with heating in hexane (~20 mL). Cooling to -15°C afforded pale yellow crystals of the dimer 2 (22.3 g, 69% yield, mp 145°C). *Anal*. Calcd: C, 59.39; H, 9.35. Found: C, 58.86; H, 9.26. Molecular weight. Found: 681 (cryscopic in benzene), 646 (mass spectrum). Calcd: 646. Major mass spectral peaks, *m/e* (relative intensity): 646(8), 631(14), 577(11), 559(20), 323(12), 308(54), 236(18), 146(11), 130(27), 73(100), 59(22), 45(32), 43(16). Proton, ^{13}C, and ^{31}P NMR data are listed in Table I.

Mesityl(trimethylsilylimino)(trimethylsilylmethylene)phosphorane (3). A sample of the dimer 2 (10.5 g, 0.016 mol) was heated under a dynamic vacuum in a flask on which was mounted a 10-cm distillation column. Some sublimation of 2 occurred along with the distillation of a colorless liquid (7.5 g, bp 91-93°C/0.03mm) which was shown by NMR to be a mixture of 2 and 3. After standing overnight at room temperature, the dimer 2 crystallized, and the supernatant liquid was removed by means of a pipette. Analysis by NMR spectroscopy (Table I) confirmed that the liquid product was compound 3 (3.3 g, 31% yield) of good purity. Complete cyrstallization to the dimer 2 occurred when the product was allowed to stand for several days at room temperature.

P-Mesityl-P-methoxy-P-(trimethylsilylmethyl)-N-(trimethylsilyl)phosphinimine (4). A freshly prepared sample of 3 (3.0 g, 9.3 mmol) was dissolved in CH_2Cl_2 (10 mL) and treated at 0°C with anhydrous methanol (0.38 mL, 9.3 mmol). After stirring for 20 min at 0°C, the mixture was allowed to warm to room temperature. Solvent removal followed by distillation gave 4 as a colorless liquid (2.8 g, 85% yield, bp 89-90°C/0.02mm). *Anal*. Calcd: C, 57.42; H, 9.64. Found: C, 57.57; H, 9.85.

P-Bromo-P-mesityl-P-(trimethylsilylmethyl)-N-(trimethylsilyl)phosphinimine (5). Using our previously reported procedure[7], phosphine 1 (37.0 g, 93 mmol) in benzene (200 mL) was treated at 0°C with a solution of bromine (16 g, 100 mmol) in benzene (75 mL). After stirring at 0°C for 4 hours, the mixture was warmed to room temperature. Removal of solvent and Me_3SiBr under reduced pressure left compound **5** as a spectroscopically pure orange liquid. Attempted distillation caused partial decomposition so that the distillate (bp 124°C/0.02mm) contained small amounts of **2** and **3** in addition to **5**. Heating of a neat sample of **5** at higher temperature (ca. 160°C) resulted in extensive decomposition to a complex mixture of products.

P-Mesityl-P-(trimethylsilylmethyl)-P-(2,2,2-trifluoroethoxy)-N-(trimethylsilyl)phosphinimine (6). A sample of the P-bromophosphinimine **5** (15.9 g, 40 mmol) was prepared as described above and was dissolved in Et_2O (60 mL). A solution of $LiOCH_2CF_3$ (40 mmol, prepared from *n*-BuLi and CF_3CH_2OH) in Et_2O (30 mL) was then added with stirring at 0°C. The mixture was warmed to room temperature and stirred overnight. Most of the Et_2O was removed under vacuum and hexane (100 mL) was added. Filtration, followed by solvent removal, and distillation gave **6** as a colorless liquid (11.0 g, 65% yield, bp 95-96°C/0.03mm). *Anal*. Calcd: C, 51.04; H, 7.85. Found: C, 52.04; H, 7.92.

PCPN Dimer, 7. A sample of the P_2N_2 dimer **2** (~2 g) was heated in a sealed, evacuated ampoule at 145°C for 2 hours. Quantitative conversion to the isomer **7** was indicated by NMR, especially ^{31}P, spectroscopy (Table I). Analytically pure crystals of **7** were obtained by recrystallization from hexane at -15°C. *Anal*. Calcd: C, 59.39; H, 9.35. Found: C, 59.01; H, 9.31. Molecular Weight. Calcd: 646. Found: 646 (mass spectrum), 613 (cryscopic in benzene). Mass spectrum. *m/e* (relative intensity): 646(4), 631(9), 559(10), 513(12), 486(17), 441(15), 411(10), 410(20), 409(10), 395(12), 368(10), 353(4), 337(10), 336(15), 324(5), 323(5), 322(5), 310(5), 309(13), 308(15), 130(20), 73(100), 59(20), 45(32). Compound 7 was also formed quantitatively when a freshly prepared sample of the monomer 3 was heated at 145°C for 2 hours in a sealed tube. Heating of 7 under a dynamic vacuum, as described above for 2, resulted only in sublimation of 7; no formation of the monomer 2 was observed.

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

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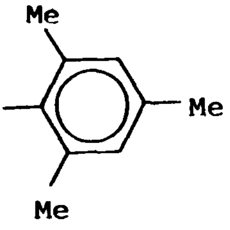
(11) Manuscript in preparation.

Table I. NMR Spectroscopic Data[a] for Mesityl-phosphorus Compounds.

R =


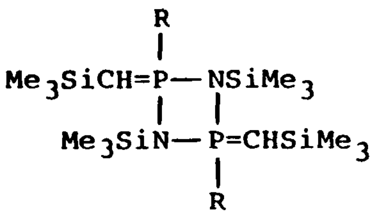
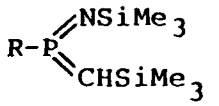
compound	signal	^1H NMR δ	^1H NMR J_{PH}	^{13}C NMR δ	^{13}C NMR J_{PC}	^{31}P NMR δ
 2	Me_3SiN	-0.23	-	2.23	4.9[b]	22.3
	Me_3SiC	0.60	-	5.59	4.2[b]	
	CH	0.63	19.8	23.25	110.5	
	o-Me	2.48	-	24.42	3.0	
				24.61	2.4	
	p-Me	2.07	-	20.71	-	
	C_6H_2	6.40	3.3	126-142[c]		
 3	Me_3SiN	-0.07	-	2.27	3.6	122.7
	Me_3SiC	0.24	-	0.94	6.1	
	CH	3.15	2.7	73.80	119.0	
	o-Me	2.60	1.7	22.68	6.5	
	p-Me	2.29	-	21.30	0.6	
	$C_6\underline{H}_2$	6.67	4.2			
	C_1			134.52	33.6	
	$C_{2,6}$			138.21	9.2	
	$C_{3,5}$			128.06	11.6	
	C_4			140.05	2.4	

Table I. continued.

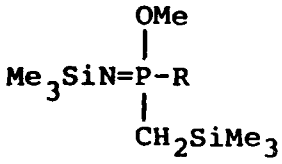
compound	signal	^1H NMR		^{13}C NMR		^{31}P NMR
		δ	J_{PH}	δ	J_{PC}	δ
 $Me_3SiN{=}\overset{\displaystyle OMe}{\underset{\displaystyle CH_2SiMe_3}{P}}{-}R$ 4	Me_3SiN	0.12	-	3.45	3.7	22.9
	Me_3SiC	0.12	-	-0.14	3.1	
	PCH_2	1.48	17.6	23.83	90.3	
	OMe	3.50	12.4	48.85	6.1	
	o-Me	2.69	1.3	22.63	3.7	
	p-Me	2.30	-	20.83	-	
	$C_6\underline{H}_2$	6.88	3.8			
	C_1			130.15	123.3	
	$C_{2,6}$			141.32	11.0	
	$C_{3,5}$			130.92	12.2	
	C_4			139.61	2.4	

Table I. continued.

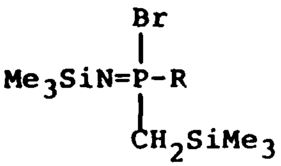
		^1H NMR		^{13}C NMR		^{31}P NMR
compound	signal	δ	J_{PH}	δ	J_{PC}	δ
 $Me_3SiN{=}P(Br)(R)CH_2SiMe_3$	Me_3SiN	0.05	-	0.14	4.2	0.8
	Me_3SiC	0.34	-	2.99	5.5	
	PCH_2	2.4[d]	-	36.57	60.4	
	o-Me	2.82	2.2	24.36	3.7	
5	p-Me	2.32	-	21.20	-	
	$C_6\underline{H}_2$	6.87	4.1			
	C_1			130.56	116.0	
	$C_{2,6}$			141.99	11.6	
	$C_{3,5}$			132.23	14.6	
	C_4			141.66	5.5	

Table I. continued.

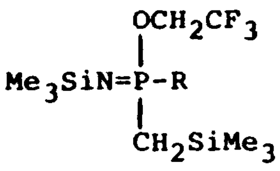
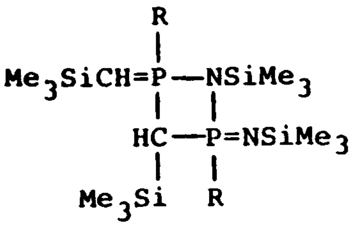
compound	signal	^1H NMR δ	^1H NMR J_{PH}	^{13}C NMR δ	^{13}C NMR J_{PC}	^{31}P NMR δ
 $Me_3SiN{=}P(OCH_2CF_3)(CH_2SiMe_3)\text{-}R$ 6	Me_3SiN	0.07	-	-0.28	3.7	23.4
	Me_3SiC	0.13	-	3.39	3.7	
	PCH_2	1.57	18.6	24.31	84.9	
	OCH_2	4.2[c]	-	59.02	4.3[e]	
	CF_3	-	-	123.32	11.6[f]	
	o-Me	2.65	1.3	23.70	3.1	
	p-Me	2.28	-	20.87	-	
	$C_6\underline{H}_2$	6.87	4.1			
	C_1			128.60	128.2	
	$C_{2,6}$			141.62	11.6	
	$C_{3,5}$			131.27	12.8	
	C_4			140.56	3.1	

Table I continued.

compound	signal	^1H NMR δ	^1H NMR J_{PH}	^{13}C NMR δ	^{13}C NMR J_{PC}	^{31}P NMR δ
	Me_3SiN	-0.28	-	1.8- 6.1[c]		10.9 -10.6[g]
		-0.16	-			
	Me_3SiC	0.55	-			
		0.60	-			
	CH	0.6[h]	-	24.2[c]		
7	PCHP	3.40	10.5[b]	52.52	34.2, 40.2	
	o-Me	2.5[c]	-	24.2[c]		
	p-Me	2.10	-	20.59	-	
	C_6H_2	6.43	4.2	126- 141[c]		

[a] Chemical shifts downfield from Me_4Si for ^1H and ^{13}C and from H_3PO_4 for ^{31}P spectra; coupling constants in Hz. Solvents: ^1H, CH_2Cl_2; ^{13}C and ^{31}P, $CDCl_3$. [b] Peaks are deceptively simple "triplets." [c] Complex multiplet with unresolved couplings and/or overlapping signals. [d] Partially hidden by p-Me signal. [e] J_{FC} = 36.6 Hz. [f] J_{FC} = 276.5 Hz. [g] J_{PP} = 15.5 Hz. [h] Partially hidden by a Me_3Si signal.