

## SYNTHESIS AND SPECTRAL PROPERTIES OF GROUP V HETEROATOM-PERMETHYLCYCLOPOLYSILANES, $\text{MeN}(\text{SiMe}_2)_n$ AND $\text{MeP}(\text{SiMe}_2)_n$

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### Summary

The permethylazacyclopolsilanes ( $\text{MeN}(\text{SiMe}_2)_n$ ,  $n = 4, 5$ ) and permethylphosphacyclopolsilanes ( $\text{MeP}(\text{SiMe}_2)_n$ ,  $n = 4, 5, 6$ ) were prepared by ring closure reactions of dichloropermethyilsilanes ( $\text{Cl}(\text{Me}_2\text{Si})_n\text{Cl}$ ,  $n = 4-6$ ) with monomethylamine and dilithium methylphosphide respectively. The permethylazacyclopolsilane  $\text{MeN}(\text{SiMe}_2)_6$  was prepared by pyrolysis of  $\text{Me}(\text{H})\text{N}(\text{SiMe}_2)_6\text{N}(\text{H})\text{Me}$  which was the initial product from the reaction of 1,6-dichlorododecamethylhexasilane with monomethylamine. Ultraviolet spectra were obtained for the nitrogen and phosphorus heterocyclic compounds and the results are compared with the data for linear and cyclic permethylpolysilanes. The  $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{31}\text{P}$  and  $^{29}\text{Si}$  NMR parameters for the permethylphosphacyclopolsilanes are reported and discussed in terms of electronic and molecular structure variations with ring size.

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### Introduction

The spectroscopic properties, e.g., UV [1], NMR [2], ESR [1] and PES [3], of cyclic polysilanes have attracted considerable attention. Much of the previous work on permethylcyclopolsilanes [4] has dealt with the nature of their bonding and in turn a description of their electronic absorption spectra. These compounds exhibit effects attributable to electron-delocalization both in ground and excited states.

It is not yet known whether the special electronic properties of cyclic polysilanes depend on all the ring atoms being identical, or whether unusual electron delocalization may also be found in polysilanes containing one or more other atoms. We decided to prepare and study the spectra of cyclic silanes containing either a nitrogen or a phosphorus atom in the ring, to see if the Group V atom would participate in any cyclic conjugation involving the silicons.

These heterocyclic compounds can be considered as model substances for elemental silicon doped with *p*-type electron donors.

Recently the preparation and characterization of heterocyclic phenylphosphapermethylsilanes,  $(\text{PhP})(\text{SiMe}_2)_n$ , ( $n = 4, 5, 6$ ), were reported [5]. However, the electronic spectra of these compounds are dominated by absorptions due to the substituted aromatic ring. Herein we report the synthesis and spectral properties of the heterocyclic compounds,  $\text{MeN}(\text{SiMe}_2)_n$  and  $\text{MeP}(\text{SiMe}_2)_n$  for  $n = 4, 5, 6$ .

## Experimental

The linear  $\alpha,\omega$ -dichloropermethylpolysilanes,  $\text{Cl}(\text{SiMe}_2)_4\text{Cl}$  and  $\text{Cl}(\text{SiMe}_2)_6\text{Cl}$ , were prepared by the chlorination of dodecamethylcyclohexasilane  $(\text{SiMe}_2)_6$  with chlorine [6,7]. The 1,5-dichloropentasilane,  $\text{Cl}(\text{SiMe}_2)_5\text{Cl}$ , was prepared similarly starting from decamethylcyclopentasilane,  $(\text{SiMe}_2)_5$  [6]. Dodecamethylcyclohexasilane,  $(\text{SiMe}_2)_6$ , was prepared by the condensation of dichlorodimethylsilane with sodium/potassium alloy [8] and decamethylcyclopentasilane,  $(\text{SiMe}_2)_5$ , prepared from it by photolysis at 2537 Å for 24 h [9]. Methylphosphine was prepared by the reduction of dimethylmethylphosphonate with lithium aluminum hydride [10].

Dimethylmethylphosphonate, monomethylamine and dichlorodimethylsilane were all commercial products. Dichlorodimethylsilane was redistilled prior to use; the others were used without further purification. *n*-Butyllithium (approximately 2 molar in hexane) was also obtained commercially and was standardized before use by quenching an aliquot of it with water and titrating with standard hydrochloric acid. Diethyl ether was dried by distillation from lithium aluminum hydride.

$^1\text{H}$  NMR spectra were recorded on a JEOL MH-100 NMR spectrometer,  $^{13}\text{C}$  spectra on a JEOL FX-60 NMR spectrometer and  $^{31}\text{P}$  and  $^{29}\text{Si}$  NMR spectra were obtained using a Varian XL-100 NMR spectrometer operating in the FT mode. Ultraviolet spectra were determined for compounds dissolved in dry deoxygenated spectrograde 2,2,4-trimethylpentane, and were recorded using a Varian Cary 118. Mass spectra were recorded on a Varian AEI MS 902. Preparative VPC was accomplished using a Varian Aerograph Model 90-P chromatograph equipped with a 3/8" × 6' QF-1 column (20% on Chromosorb W, 60–80 mesh). Elemental analyses were performed by M.H.W. Laboratories, Phoenix, Arizona and Galbraith Laboratories, Knoxville, Tennessee.

All manipulations were carried out under inert atmosphere using standard Schlenk techniques with oven dried glassware [11]. All the Group V-silicon heterocycles reported here are extremely sensitive to oxygen and moisture. The phosphorus-silicon heterocycles will inflame in air when spread on a piece of tissue paper.

### *Preparation of dilithium methylphosphide*

Dilithium methylphosphide was prepared *in situ* by condensing methylphosphine into a Schlenk tube containing a degassed diethyl ether solution of two equiv of *n*-butyllithium at  $-196^\circ\text{C}$ . The mixture was allowed to warm slowly to  $0^\circ\text{C}$  at which point a yellow slurry of dilithium methylphosphide formed.

The slurry was stirred for one hour at room temperature under an atmosphere of nitrogen prior to use.

#### Preparation of $\text{MeP}(\text{SiMe}_2)_n$ ( $n = 4, 5, 6$ )

A solution of the dichloropermethylpolysilane  $\text{Cl}(\text{SiMe}_2)_n\text{Cl}$  ( $n = 4, 5, 6$ ) in approximately 50 ml of diethyl ether was added dropwise under an atmosphere of nitrogen to a slurry of freshly prepared dilithium methylphosphide in 150 ml of diethyl ether at approximately  $-40^\circ\text{C}$  (acetonitrile/dry ice slush). Upon completion of the addition, the resulting solution was slowly warmed to room temperature and stirred overnight to ensure the completion of the reaction. The solution was then concentrated to approximately 50 ml and filtered to remove the lithium chloride. The remaining solvent was then distilled off leaving a pale yellow oil which was distilled in vacuo through a 15 cm Vigreux column.

$\text{MeP}(\text{SiMe}_2)_6$ . Using the above procedure, the reaction of  $\text{Cl}(\text{SiMe}_2)_6\text{Cl}$  (6.09 g, 14.5 mmol) with  $\text{MePLi}_2$  (from 14.5 mmol  $\text{MePH}_2$ ) yielded  $\text{MeP}(\text{SiMe}_2)_6$  (3.12 g, 7.92 mmol, yield 54%) as a colorless waxy solid, b.p.  $110-112^\circ\text{C}/0.05$  Torr. Anal. Found: C, 39.48; H, 9.84; P, 7.83.  $\text{C}_{13}\text{H}_{39}\text{PSi}_6$  calcd.: C, 39.54; H, 9.95; P, 7.84%.

$\text{MeP}(\text{SiMe}_2)_5$ . Using the above procedure, the reaction of  $\text{Cl}(\text{SiMe}_2)_5\text{Cl}$  (6.79 g, 18.8 mmol) with  $\text{MePLi}_2$  (from 18.8 mmol  $\text{MePH}_2$ ) yielded  $\text{MeP}(\text{SiMe}_2)_5$  (3.27 g, 9.73 mmol, yield 51%) as a waxy solid, b.p.  $81-85^\circ\text{C}/0.05$  Torr. Anal. Found: C, 39.23; H, 9.88; P, 9.20.  $\text{C}_{11}\text{H}_{33}\text{PSi}_5$  calcd.: C, 38.87; H, 10.07; P, 9.75%. High resolution mass number. Found: 336.1154,  $\text{C}_{11}\text{H}_{33}\text{PSi}_5$  calcd.: 336.1166, dev.  $-3.7$  ppm.

$\text{MeP}(\text{SiMe}_2)_4$ . Using the above procedure, the reaction of  $\text{Cl}(\text{SiMe}_2)_4\text{Cl}$  (5.00 g, 16.5 mmol) with  $\text{MePLi}_2$  (from 16.5 mmol  $\text{MePH}_2$ ) yielded  $\text{MeP}(\text{SiMe}_2)_4$  (2.10 g, 7.55 mmol, yield 46%) as a colorless liquid, b.p.  $56-59^\circ\text{C}/0.05$  Torr. High resolution mass number Found: 278.0926,  $\text{C}_9\text{H}_{27}\text{PSi}_4$  calcd.: 278.0927. Dev.  $-0.1$  ppm.

#### Preparation of $\text{MeN}(\text{SiMe}_2)_n$ ( $n = 4, 5$ )

Monomethylamine was condensed dropwise by means of a dry ice cold finger into a solution of the dichloropermethylpolysilane  $\text{Cl}(\text{SiMe}_2)_n\text{Cl}$  ( $n = 4, 5$ ) in approximately 150 ml of diethyl ether at room temperature. A flocculant white precipitate,  $\text{MeNH}_3\text{Cl}$ , formed immediately. The solution was stirred overnight to ensure completion of the reaction. The mixture was then refluxed to coagulate the precipitate. The mixture was cooled and filtered, and the solution concentrated in vacuo. The desired product was isolated by preparative VPC.

$\text{MeN}(\text{SiMe}_2)_4$ . Using the above procedure, the reaction of  $\text{Cl}(\text{SiMe}_2)_4\text{Cl}$  with  $\text{MeNH}_2$  yielded  $\text{MeN}(\text{SiMe}_2)_4$  as a colorless viscous oil. High resolution mass number Found: 261.1221,  $\text{C}_9\text{H}_{27}\text{NSi}_4$  calcd.: 261.1221, Dev. 0.0 ppm.

$\text{MeN}(\text{SiMe}_2)_5$ . Using the same procedure, the reaction of  $\text{Cl}(\text{SiMe}_2)_5\text{Cl}$  with  $\text{MeNH}_2$  yielded  $\text{MeN}(\text{SiMe}_2)_5$  as a white solid. High resolution mass number Found: 319.1458,  $\text{C}_{11}\text{H}_{33}\text{NSi}_5$  calcd.: 319.1459. Dev.  $-0.2$  ppm.

#### Preparation of $\text{MeN}(\text{H})(\text{SiMe}_2)_6\text{N}(\text{H})\text{Me}$

Monomethylamine was condensed dropwise by means of a dry ice cold

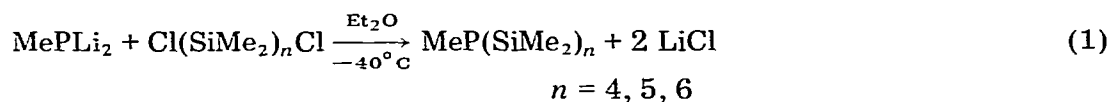
finger into a solution of  $\text{Cl}(\text{SiMe}_2)_6\text{Cl}$  (7.38 g, 17.6 mmol) in 150 ml of diethyl ether. A white precipitate,  $\text{MeNH}_3\text{Cl}$ , formed immediately. The mixture was stirred overnight at room temperature to ensure completion of the reaction. The mixture was then filtered and the solvent removed by distillation leaving a viscous oil which was distilled in vacuo through a 15 cm Vigreux column to give  $\text{MeN}(\text{H})(\text{SiMe}_2)_6\text{N}(\text{H})\text{Me}$  (6.23 g, 15.3 mmol, yield 86%) as a colorless liquid, b.p.  $117\text{--}120^\circ\text{C}/0.1$  Torr. Anal. Found: C, 40.95; H, 10.74; N, 6.66.  $\text{C}_{14}\text{H}_{44}\text{N}_2\text{Si}_6$  calcd.: C, 41.10; H, 10.86; N, 6.85%.

#### Preparation of $\text{MeN}(\text{SiMe}_2)_6$

A neat sample of  $\text{MeNH}(\text{SiMe}_2)_6\text{NHMe}$  was pyrolyzed at  $290^\circ\text{C}$  for 4 h in a Schlenk tube under argon. At the end of this period the clear liquid starting material had become waxy in appearance. By GC analysis,  $\text{MeN}(\text{SiMe}_2)_6$  was formed in good yield and isolated by preparative VPC. High resolution mass number Found: 377.1710,  $\text{C}_{13}\text{H}_{39}\text{NSi}_6$  calcd.: 377.1698, Dev. 1.2 ppm.

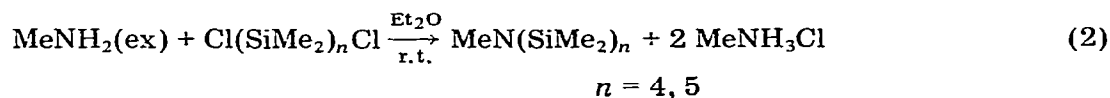
#### Results and discussion

The reactions of 1,4-, 1,5- and 1,6-dichloropermethylpolysilanes  $\text{Cl}(\text{SiMe}_2)_n\text{Cl}$  ( $n = 4, 5, 6$ ) with dilithium methylphosphide in diethyl ether at  $-40^\circ\text{C}$  yield respectively the 5-, 6- and 7-membered heterocycles containing one phosphorus atom (eq. 1):

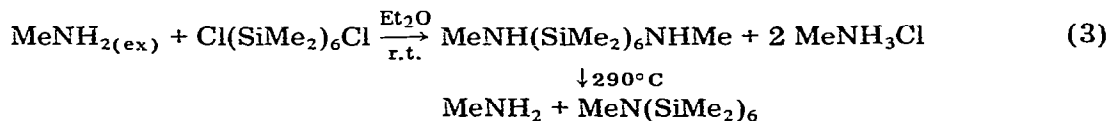


The products of these reactions were isolated in moderate yields by vacuum distillation.

The reactions of 1,4- and 1,5-dichloropermethylpolysilanes with monomethylamine in diethyl ether at room temperature yield respectively the 5- and 6-membered ring closure products directly (eq. 2):



In contrast the reaction of 1,6-dichlorododecamethylhexasilane  $\text{Cl}(\text{SiMe}_2)_6\text{Cl}$  with monomethylamine in diethyl ether at room temperature yields the linear product 1,6-bis(methylamino)dodecamethylhexasilane. Pyrolysis of this species at  $290^\circ\text{C}$  for 4 h under argon gave the 7-membered heterocycle  $\text{MeN}(\text{SiMe}_2)_6$  (eq. 3):



This result is analogous to the pyrolysis of  $\text{MeNH}(\text{SiPh}_2)_4\text{NHMe}$  which was reported to yield  $\text{MeN}(\text{SiPh}_2)_4$  [12]. The reactions of 1,4-, 1,5- and 1,6- dichloropermethylpolysilanes  $\text{Cl}(\text{SiMe}_2)_n\text{Cl}$  ( $n = 4, 5, 6$ ) with monomethylamine

provide an interesting demonstration of the ease of ring closure to form 5- and 6-membered rings compared with the 7-membered ring.

#### *Ultraviolet spectra and delocalization*

The ultraviolet absorption data for the nitrogen-silicon and phosphorus-silicon heterocycles prepared in this work are summarized in Table 1, together with comparison data for permethylcyclopolysilanes and linear permethylpolysilanes. A bathochromic shift is observed for the nitrogen heterocyclic compounds with increasing ring size, quite similar to the trend found for the linear permethylpolysilanes. However, the phosphorus-silicon heterocycles resemble the cyclic polysilanes rather than the linear polysilanes, in that both  $\text{MeP}(\text{SiMe}_2)_4$  and  $(\text{Me}_2\text{Si})_5$  have a low-intensity absorption at unusually long wavelength (Fig. 1).

The ultraviolet absorption bands of permethylpolysilanes are generally explained as due to either  $\sigma-\sigma^*$  or  $\sigma-\pi$  transitions, and the low-energy electronic transitions for the nitrogen- and phosphorus-containing silanes are probably similar in origin. The other electrons which might be involved in electronic absorption are the lone pair ( $n$ ) orbitals of the heteroatoms, but photoelectron spectroscopic data [15] for related compounds indicate that these lone pair orbitals should lie somewhat below the  $\sigma(\text{Si}-\text{Si})$  orbitals in energy.

Thus for the nitrogen heterocyclic compounds it is tempting to rationalize

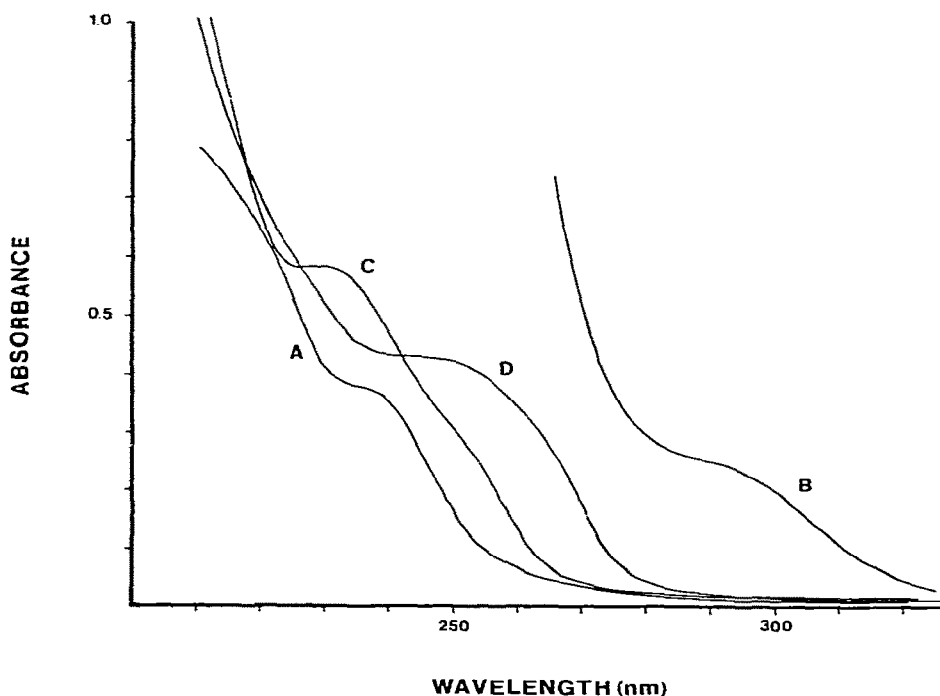


Fig. 1. Ultraviolet absorption spectra for  $\text{MeP}(\text{SiMe}_2)_n$  ( $n = 4, 5, 6$ ): A,  $\text{MeP}(\text{SiMe}_2)_4$ ,  $6.36 \times 10^{-4} M$ ; B,  $\text{MeP}(\text{SiMe}_2)_4$ ,  $3.85 \times 10^{-3} M$ ; C,  $\text{MeP}(\text{SiMe}_2)_5$ ,  $9.66 \times 10^{-4} M$ ; D,  $\text{MeP}(\text{SiMe}_2)_6$ ,  $6.00 \times 10^{-4} M$ . At higher concentrations no long wavelength transitions were observed for  $\text{MeP}(\text{SiMe}_2)_n$  ( $n = 5, 6$ ).

TABLE 1

ULTRAVIOLET SPECTRAL DATA FOR THE GROUP V HETEROATOM PERMETHYLCYCLOPOLY-SILANES AND RELATED COMPOUNDS

Compound	$\lambda_{\max}$	$\epsilon$	Ref.
MeN(SiMe <sub>2</sub> ) <sub>4</sub>	235	4000	this work
	210	9000	this work
MeN(SiMe <sub>2</sub> ) <sub>5</sub>	242	1900	this work
	214	8800	this work
MeN(SiMe <sub>2</sub> ) <sub>6</sub>	249	2500	this work
	228	8500	this work
MeP(SiMe <sub>2</sub> ) <sub>4</sub>	277	530	this work
	234	6000	this work
	210	12000	this work
MeP(SiMe <sub>2</sub> ) <sub>5</sub>	249	3600	this work
	226	5900	this work
MeP(SiMe <sub>2</sub> ) <sub>6</sub>	261	5300	this work
	242	7000	this work
	210	10000	this work
(Me <sub>2</sub> Si) <sub>5</sub>	275	700	13
	265	800	13
	210	24000	13
(Me <sub>2</sub> Si) <sub>6</sub>	260	1070	13
	236	5700	13
	197	43800	13
(Me <sub>2</sub> Si) <sub>7</sub>	249	3600	13
	239	4600	13
	221	9200	13
Me(Me <sub>2</sub> Si) <sub>4</sub> Me	235	14700	14
Me(Me <sub>2</sub> Si) <sub>5</sub> Me	250	18470	14
Me(Me <sub>2</sub> Si) <sub>6</sub> Me	260	21100	14
	220	14000	14

the UV spectra in terms of localized polysilane transitions, to which the heteroatom makes little contribution. The extinction coefficients for these compounds are lower than for the linear polysilanes, consistent with a  $\sigma-\sigma^*$  transition polarized along the molecular axis for the linear compounds and hence constrained in the heterocycles [16].

In order to analyze the effect of the phosphorus atom on the electronic transitions in the heterocycles, it is helpful to compare the HOMO and excited-state energies of these compounds with those for the cyclosilanes. The HOMO energies are available from photoelectron spectra, and the relative energies of the first singlet excited state are then estimated from the energy of the longest-wavelength transition. Results are shown schematically in Fig. 2. The presence of the phosphorus atom shifts the HOMO energy downward, by 0.2 to 0.3 eV, in both the 5- and 6-membered rings. This is consistent with the higher electronegativity of phosphorus than silicon, and indicates that the inductive effect of the heteroatom is dominant over any dative back-bonding which may take place from the lone pair on phosphorus to silicon.

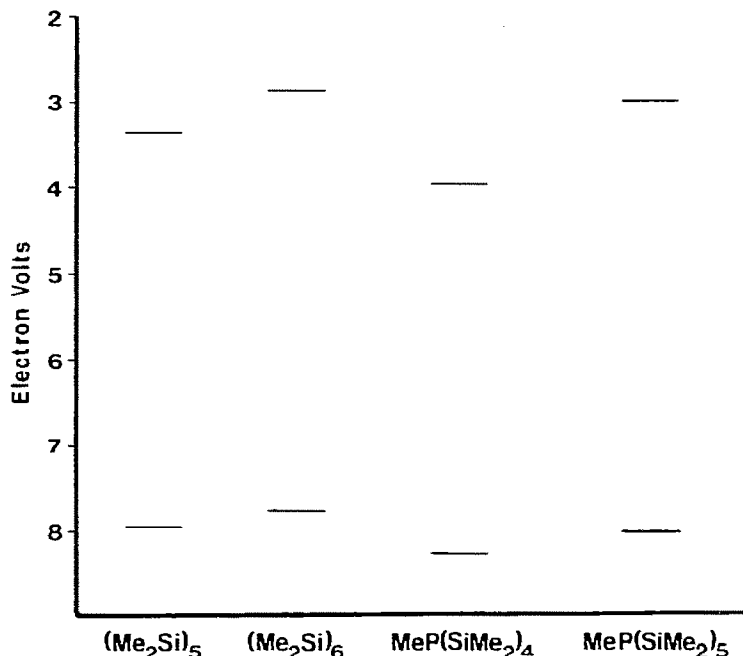


Fig. 2. Diagram of the HOMO and first excited state energies for (Me<sub>2</sub>Si)<sub>5</sub>, (Me<sub>2</sub>Si)<sub>6</sub>, MeP(SiMe<sub>2</sub>)<sub>4</sub>, MeP(SiMe<sub>2</sub>)<sub>5</sub>.

The first excited state for MeP(SiMe<sub>2</sub>)<sub>5</sub> is slightly stabilized compared to (Me<sub>2</sub>Si)<sub>6</sub>. The energy difference upon introducing a phosphorus atom into the 6-membered ring is less for the excited state than for the HOMO, consistent with inductive perturbation by the electronegative heteroatom. However for MeP(SiMe<sub>2</sub>)<sub>4</sub>, the excited state is greatly stabilized compared with that for either (Me<sub>2</sub>Si)<sub>5</sub> or MeP(SiMe<sub>2</sub>)<sub>5</sub>.

The unusually low-energy excited state for (Me<sub>2</sub>Si)<sub>5</sub> has been tentatively explained as due to excitation into a LUMO of  $\pi$ -type, stabilized by favorable orbital overlap in the nearly planar 5-membered silane ring [4]. If this explanation is correct, our results indicate that such conjugation occurs also in MeP(SiMe<sub>2</sub>)<sub>4</sub>, but not in MeN(SiMe<sub>2</sub>)<sub>4</sub>. Perhaps phosphorus, being a second-row atom, has orbitals of appropriate energy to contribute to the LUMO whereas nitrogen does not. Determinations of the photoelectron and UV spectra of other 5-membered rings containing silicon and other heteroatoms will be needed to explain these effects more fully.

#### <sup>1</sup>H, <sup>13</sup>C, <sup>31</sup>P, <sup>29</sup>Si NMR spectra

<sup>1</sup>H, <sup>13</sup>C, <sup>31</sup>P and <sup>29</sup>Si NMR data for the compounds prepared are presented in Tables 2 and 3. A single <sup>1</sup>H and <sup>13</sup>C resonance is observed for all the geminal methyl groups in these molecules; therefore, these nitrogen-silicon and phosphorus-silicon heterocycles exhibit rapid conformational equilibration at room temperature. The <sup>1</sup>H and <sup>13</sup>C chemical shifts of the methyl groups are consistent with the trend expected by the replacement of a silicon atom of a cyclic

TABLE 2

<sup>1</sup>H AND <sup>13</sup>C NMR PARAMETERS OF THE NITROGEN-SILICON HETEROCYCLES, MeN(SiMe<sub>2</sub>)<sub>n</sub> AND MeNH(SiMe<sub>2</sub>)<sub>6</sub>NHMe

Compound	SiMe <sub>2</sub> group <sup>a</sup>	<sup>1</sup> H <sup>b</sup>	<sup>13</sup> C <sup>b</sup>
MeN(SiMe <sub>2</sub> ) <sub>4</sub>	—	2.45	—
	α	0.23	-0.50
	β	0.20	-7.23
MeN(SiMe <sub>2</sub> ) <sub>5</sub>	—	2.47	—
	α	0.31	0.16
	β	0.29	-5.69
	γ	0.26	-6.24
MeN(SiMe <sub>2</sub> ) <sub>6</sub>	—	2.48	—
	α	0.38	—
	β	0.34	—
	γ	0.34	—
MeNH(SiMe <sub>2</sub> ) <sub>6</sub> NHMe	—	2.28 (d, J 6.0)	—
	α	0.37	—
	β	0.31	—
	γ	0.27	—
	—	—	—

<sup>a</sup> SiMe<sub>2</sub> groups are lettered alphabetically from the nitrogen atom. <sup>b</sup> δ (ppm), in C<sub>6</sub>D<sub>6</sub> solution, reference internal TMS.

polysilane with a more electronegative nitrogen or phosphorus. The resonances of the methyl groups move downfield as their distance from the electronegative heteroatom decreases.

The trend observed for the <sup>29</sup>Si chemical shifts can be interpreted similarly. The resonances of the α-silicon atoms are shifted downfield due to deshielding by the adjacent heteroatom while the chemical shifts of the β- and γ-silicon atoms are only slightly different from those observed for permethylcyclopolysilanes.

TABLE 3

<sup>1</sup>H, <sup>13</sup>C, <sup>31</sup>P, <sup>29</sup>Si NMR PARAMETERS OF THE PHOSPHORUS-SILICON HETEROCYCLES MeP(SiMe<sub>2</sub>)<sub>n</sub>

Compound	<sup>31</sup> P <sup>a</sup>	SiMe <sub>2</sub> group <sup>b</sup>	<sup>1</sup> H <sup>c</sup>	<sup>13</sup> C{ <sup>1</sup> H} <sup>c</sup>	<sup>29</sup> Si{ <sup>1</sup> H} <sup>d</sup>
MeP(SiMe <sub>2</sub> ) <sub>4</sub>	-103.1	α	0.39 (5.0)	-2.43 (15.0)	-8.24 (35.4)
		β	0.32	-5.36	-41.67 (1.0)
MeP(SiMe <sub>2</sub> ) <sub>5</sub>	-104.3	α	0.29 (5.5)	-2.10 (11.6)	-16.67 (43.0)
		β	0.22	-5.55 (2.5)	-43.37 (14.5)
		γ		-5.74	-42.87 (2.5)
MeP(SiMe <sub>2</sub> ) <sub>6</sub>	-103.9	α	0.28 (4.0)	-1.68 (7.5)	-15.95 (50.0)
		β	0.26	-5.02 (3.3)	-42.80 (19.1)
		γ		-5.13	-42.16 (4.5)

<sup>a</sup> δ (ppm), in C<sub>6</sub>D<sub>6</sub> solution, reference external H<sub>3</sub>PO<sub>4</sub>. Chemical shifts upfield of H<sub>3</sub>PO<sub>4</sub> have a negative sign. <sup>b</sup> SiMe<sub>2</sub> groups are lettered alphabetically from the phosphorus atom. <sup>c</sup> δ (ppm), in C<sub>6</sub>D<sub>6</sub> solution, reference C<sub>6</sub>D<sub>5</sub>H. J(PH) and J(PC) (in parentheses) are reported in Hertz. Phosphorus methyl group not included. <sup>d</sup> δ (ppm), in C<sub>6</sub>D<sub>6</sub> solution, reference external TMS. J(PSi) (in parentheses) are reported in Hertz.



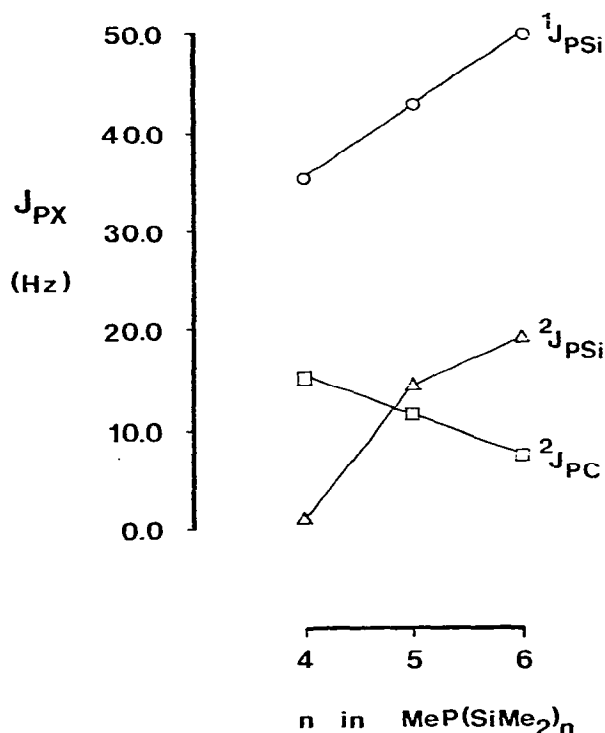


Fig. 3.  $^1J(\text{PSi})$ ,  $^2J(\text{PSi})$  and  $^2J(\text{PC})$  coupling constants of  $\text{MeP}(\text{SiMe}_2)_n$  as a function of ring size  $n$ .

Interestingly, the  $^{31}\text{P}$  chemical shifts of  $\text{MeP}(\text{SiMe}_2)_n$  ( $n = 4, 5, 6$ ) are nearly identical. In contrast a large chemical shift difference was observed between the phospholane  $\text{MeP}(\text{CH}_2)_4$  ( $\delta(\text{P}) -32$  ppm) [17] and the phosphorinane  $\text{MeP}(\text{CH}_2)_5$  ( $\delta(\text{P}) -53.7$  ppm) [18] which has been attributed to the steric influence of the  $\gamma$ -carbon atom in the 6-membered ring [17]. In the phenylphosphapermethylsilanes ( $\text{PhP}(\text{SiMe}_2)_n$ ,  $n = 4, 5, 6$ ), a small increase in shielding was observed along the series [5] which was attributed to the net result of the opposing effects of angular variations and  $\gamma$ -steric interactions. Evidently these two effects exactly cancel each other in the permethylphosphacyclopolyisilane series  $\text{MeP}(\text{SiMe}_2)_n$  ( $n = 4, 5, 6$ ).

The dependence of the coupling constants  $J(\text{PX})$  ( $X = \text{C}, \text{Si}$ ) (Fig. 3) on ring size parallels the trend observed previously [5] for the heterocyclic phenylphosphapermethylsilanes. The values of  $^1J(\text{PSi})$  and  $^2J(\text{PSi})$  increase steadily with ring size while the value of  $^2J(\text{PC})$  decreases with increasing ring size. If a Fermi contact interaction is assumed to provide the major contribution to the coupling constants [19] then the increasing values of  $^1J(\text{PSi})$  and  $^2J(\text{PSi})$  observed with increasing ring size can be interpreted as the result of increased Si-P-Si bond angles. Similarly the decrease in  $^2J(\text{PC})$  along the series  $\text{MeP}(\text{SiMe}_2)_n$  ( $n = 4, 5, 6$ ) can be attributed to the expected decrease in the P-Si-C angle with increasing ring size.

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