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**SYNTHESIS AND DYNAMIC NUCLEAR MAGNETIC RESONANCE STUDIES OF THE HETEROCYCLIC DIPHOSPHACYCLOPOLYSILANES,  $(\text{PhP})_2(\text{SiMe}_2)_n$ . CRYSTAL AND MOLECULAR STRUCTURE OF  $(\text{PhP})_2(\text{SiMe}_2)_3$  \***

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### Summary

The heterocyclic diphosphanes  $(\text{PhP})_2(\text{SiMe}_2)_n$  ( $n = 2, 3, 4$ ) were synthesized by the reactions of 1,2-dilithium-1,2-diphenyldiphosphide with  $\alpha,\omega$ -dichloropermethylpolysilanes  $\text{Cl}(\text{SiMe}_2)_n\text{Cl}$  ( $n = 2, 3, 4$ ). Stereochemical fluxionality in these compounds was examined by dynamic nuclear magnetic resonance. The  $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{31}\text{P}$  and  $^{29}\text{Si}$  NMR spectra are reported and discussed in terms of a phosphorus inversion mechanism. Values of the free energy of activation for phosphorus inversion are reported for  $(\text{PhP})_2(\text{SiMe}_2)_n$  ( $n = 3, 4$ ) and compared with related compounds.

A single-crystal X-ray structure analysis has been carried out on  $(\text{PhP})_2(\text{SiMe}_2)_3$ . The material crystallizes in the monoclinic space group  $P2_1/c$  with four molecules per unit cell. The cell dimensions are  $a = 12.526(11)$  Å,  $b = 11.828(10)$  Å,  $c = 15.412(7)$  Å and  $\beta = 103.56(6)^\circ$ . The molecule exists in the *dl* (*trans*) form with the five-membered ring significantly twisted. The angle between the phosphorus–phosphorus bond and the plane of the three silicon atoms is  $42.9^\circ$ .

### Introduction

The stereochemical fluxionality of diphosphines of the type  $\text{RCH}_3\text{PPCH}_3\text{R}$  has been studied in some detail [1,2]. The results have been interpreted in terms of an interconversion between the *meso* and *dl* forms. The mechanism of interconversion involves an inversion of configuration at phosphorus and a rotation about the phosphorus–phosphorus bond. The free energy of activation,  $\Delta G^\ddagger$ , for this process is in the range of 23 kcal/mol [2].

Several silicon-substituted diphosphines have been reported previously [3,4]. However unlike the tetraalkyldiphosphines, 1,2-diphenyl-1,2-bis(trimethylsilyl)-

\* This article is dedicated to Professor Henry Gilman, to whom all of us who work in organosilicon chemistry owe so much, with warm personal wishes from R.W.

diphosphine,  $\text{Ph}(\text{Me}_3\text{Si})\text{PP}(\text{SiMe}_3)\text{Ph}$ , was found to exist only in the *meso* form (*trans* conformation), i.e., only one resonance was observed for the methyl hydrogens in the  $^1\text{H}\{^{31}\text{P}\}$  NMR spectrum.

In this paper we report the synthesis and dynamic nuclear magnetic resonance studies of the diphosphacyclopolyasilanes,  $(\text{PhP})_2(\text{SiMe}_2)_n$  ( $n = 2,3,4$ ). These compounds provide interesting comparisons with previous work on the effect of silicon substitution and ring size on phosphorus inversion in diphosphines. In addition we have determined the X-ray crystal structure of  $(\text{PhP})_2(\text{SiMe}_2)_3$  in order to establish its solid state conformation.

### Experimental

The linear  $\alpha,\omega$ -dichloropermethylpolysilanes,  $\text{Cl}(\text{SiMe}_2)_n\text{Cl}$  ( $n = 2,3,4$ ) were prepared by the chlorination of dodecamethylcyclohexasilane  $(\text{SiMe}_2)_6$  with chlorine [5,6]. Dodecamethylcyclohexasilane  $(\text{SiMe}_2)_6$  was prepared by the condensation of dichlorodimethylsilane with sodium-potassium alloy [7]. Phenylphosphine was synthesized by the reduction of dichlorophenylphosphine with lithium aluminum hydride [8]. Pentaphenylcyclopentaphosphine  $(\text{PhP})_5$  was prepared by the reaction of phenylphosphine with dichlorophenylphosphine [9].

Dichlorodimethylsilane, dichlorophenylphosphine, Na/K alloy and lithium were all commercial products. The dichlorodimethylsilane was redistilled prior to use. Tetrahydrofuran was dried by distillation from lithium aluminium hydride.

$^1\text{H}$ ,  $^{31}\text{P}$  and  $^{29}\text{Si}$  NMR spectra were obtained using a Varian XL-100 NMR spectrometer operating in the FT mode and  $^{13}\text{C}$  spectra were recorded on a JEOL FX-60 NMR spectrometer. Elemental analyses were performed by M.H.W. Laboratories, Phoenix, Arizona.

All manipulations were carried out under inert atmosphere using standard Schlenk techniques. The phosphasilanes reported here are extremely sensitive to oxygen and moisture.

#### *Preparation of 1,2-dilithium-1,2-diphenyldiphosphide*

Activated lithium was prepared by the slow evaporation of ammonia from a solution of Li (0.28 g Li wire, 0.040 mol) in approximately 25 ml of liquid ammonia. Pentaphenylcyclopentaphosphine (4.32 g/0.008 mol) was added all at once to the activated Li in 50 ml of tetrahydrofuran. Although an orange slurry formed immediately, the mixture was refluxed for three hours to ensure completion of the reaction. The orange slurry was diluted with 250 ml of tetrahydrofuran prior to use.

#### *Preparation of $(\text{PhP})_2(\text{SiMe}_2)_4$ (I)*

A solution of  $\text{Cl}(\text{SiMe}_2)_4\text{Cl}$  (6.06 g, 0.020 mol) in 50 ml of tetrahydrofuran was added dropwise to the slurry of 1,2-dilithium-1,2-diphenyldiphosphide at  $-78^\circ\text{C}$ . Upon completion of the addition, the resulting colorless solution was allowed to warm slowly to room temperature and was stirred overnight. The solution was concentrated to approximately 50 ml and filtered to remove the lithium chloride. The solvent that remained was removed by distillation leaving an off-white waxy material. Distillation in vacuo through a 15 cm Vigreux column afforded the product  $(\text{PhP})_2(\text{SiMe}_2)_4$  (4.11 g, 46%) as a white waxy solid, b.p.  $160\text{--}164^\circ\text{C}/0.05$  Torr. Anal. Found: C, 53.68; H, 7.35; P, 13.88.  $\text{C}_{20}\text{H}_{34}\text{P}_2\text{Si}_4$  calcd.: C, 53.57; H, 7.59; P, 13.84% .

*Preparation of (PhP)<sub>2</sub>(SiMe<sub>2</sub>)<sub>3</sub> (II)*

The procedure used for synthesis and purification followed that given for  $(\text{PhP})_2(\text{SiMe}_2)_4$ . 1,2-Dilithium-1,2-diphenyldiphosphide prepared as described above was treated with  $\text{Cl}(\text{SiMe}_2)_3\text{Cl}$  (4.90 g, 0.020 mol) yielding after workup

TABLE 1

FINAL ATOM COORDINATES ( $\times 10^4$ ) FOR II (E.S.D.'S IN PARENTHESES)

Atom	x	y	z
(1)	1774(1)	368(1)	13(1)
(2)	3241(1)	1237(1)	-213(1)
I(1)	2742(1)	1139(1)	-1736(1)
I(2)	2419(1)	-810(1)	-1940(1)
I(3)	2162(1)	-1324(1)	-531(1)
(1a)	2141(2)	84(2)	1227(2)
(2a)	3155(3)	285(3)	1780(2)
(3a)	3357(3)	52(4)	2687(2)
(4a)	2538(3)	-375(3)	3044(2)
(5a)	1531(3)	-574(3)	2505(2)
(6a)	1320(3)	-340(3)	1596(2)
(1b)	2945(2)	2720(2)	16(2)
(2b)	1920(3)	3135(3)	34(3)
(3b)	1782(3)	4244(3)	262(3)
(4b)	2656(3)	4958(3)	468(2)
(5b)	3665(3)	4571(3)	440(2)
(6b)	3817(3)	3466(3)	222(2)
(7)	1502(3)	2012(3)	-2214(2)
(8)	3935(3)	1671(3)	-2149(2)
(9)	1157(3)	-1133(3)	-2836(2)
(10)	3659(3)	-1533(3)	-2171(2)
(11)	961(3)	-2261(3)	-533(2)
(12)	3437(3)	-1948(3)	191(2)
H(2a)	3724	594	1541
H(3a)	4062	188	3060
H(4a)	2668	-531	3664
H(5a)	958	-877	2746
H(6a)	607	-474	1228
H(2b)	1298	2650	-115
H(3b)	1066	4507	273
H(4b)	2552	5720	628
H(5b)	4275	5071	573
H(6b)	4533	3209	212
H(7a)	1320	1949	-2847
H(7b)	1672	2792	-2116
H(7c)	894	1741	-2003
H(8a)	3762	1643	-2784
H(8b)	4014	2459	-2046
H(8c)	4563	1223	-1906
H(9a)	1060	-1928	-2894
H(9b)	1272	-920	-3401
H(9c)	540	-759	-2705
H(10a)	3519	-2319	-2253
H(10b)	3748	-1314	-2743
H(10c)	4286	-1357	-1711
H(11a)	927	-2421	63
H(11b)	1085	-2985	-757
H(11c)	317	-1940	-901
H(12a)	3307	-2147	754
H(12b)	3586	-2656	-47
H(12c)	4045	-1469	189

and distillation  $(\text{PhP})_2(\text{SiMe}_2)_3$  (4.37 g, 56%) as a white solid, bp 155–160°C/0.1 Torr, m.p. 153–156°C. Anal. Found: C, 55.52; H, 7.40; P, 15.46.  $\text{C}_{18}\text{H}_{28}\text{P}_2\text{Si}_3$  calcd.: C, 55.35; H, 7.23; P, 15.86%.

#### Preparation of $(\text{PhP})_2(\text{SiMe}_2)_2$ (III)

Using the above procedure, the reaction of  $\text{Cl}(\text{SiMe}_2)_2\text{Cl}$  (3.74 g, 0.020 mol) with the slurry of 1,2-dilithium-1,2-diphenyldiphosphide yielded  $(\text{PhP})_2(\text{SiMe}_2)_2$  (1.05 g, 3.16 mmol, yield 16%) as a white solid, b.p. 190–195°C/0.08 Torr. Anal. Found: C, 57.61; H, 6.57; P, 18.41.  $\text{C}_{16}\text{H}_{22}\text{P}_2\text{Si}_2$  calcd.: C, 57.79; H, 6.68, P, 18.63%.

#### Crystal structure of $(\text{PhP})_2(\text{SiMe}_2)_3$

A crystal of the compound was obtained by slow evaporation from a solution of benzene and hexane (1/1 v/v). The crystal chosen for the X-ray study had dimensions 0.20 × 0.50 × 1.05 mm and was sealed in a glass capillary under inert atmosphere. The crystal was mounted on a Syntex P1 autodiffractometer equipped with a graphite-monochromated  $\text{Mo-K}_\alpha$  source. After careful crystal alignment 15 diffraction maxima were used to obtain orientation and cell parameters. The compound is monoclinic with space group  $P2_{1/c}$  and cell dimensions  $a = 12.526(11)$  Å,  $b = 11.828(10)$  Å,  $c = 15.412(7)$  Å and  $\beta = 103.56(6)^\circ$ . For  $z = 4$  the calculated density is 1.14 g/ml.

Data points numbering 4330 were collected from  $3^\circ \leq 2\theta \leq 50^\circ$  and merged to give 3919 unique reflections of which 3194 had  $I \geq 2\sigma(I)$  and were used in the structure analysis. The data were treated in the usual fashion for Lorentz-

TABLE 2

ANISOTROPIC THERMAL PARAMETERS ( $\times 10^4$ ) FOR II (E.S.D.'s IN PARENTHESES)

Atom	$U_{11}$	$U_{22}$	$U_{33}$	$U_{12}$	$U_{13}$	$U_{23}$
P(1)	369(4)	412(4)	361(4)	-12(3)	106(3)	0(3)
P(2)	374(4)	395(4)	426(4)	-17(3)	134(3)	-17(3)
Si(1)	426(5)	392(4)	407(4)	-16(3)	136(3)	13(3)
Si(2)	478(5)	409(4)	388(4)	-33(4)	167(4)	-29(3)
Si(3)	409(4)	376(4)	391(4)	-30(3)	126(3)	4(3)
C(1a)	430(16)	396(15)	362(15)	22(12)	118(12)	-10(12)
C(2a)	549(21)	831(25)	443(18)	-151(18)	84(16)	16(17)
C(3a)	725(25)	1005(31)	431(19)	-114(22)	-59(18)	-4(19)
C(4a)	963(30)	727(24)	383(18)	42(22)	163(19)	36(17)
C(5a)	736(25)	940(28)	474(19)	-66(21)	267(18)	146(19)
C(6a)	481(18)	688(22)	494(18)	-27(16)	146(15)	84(16)
C(1b)	474(17)	408(16)	358(15)	-8(13)	136(13)	-29(12)
C(2b)	558(21)	498(20)	982(28)	-60(16)	347(20)	-151(19)
C(3b)	744(26)	555(22)	1115(33)	71(19)	492(24)	-165(22)
C(4b)	955(28)	394(18)	497(22)	-27(19)	301(20)	-69(15)
C(5b)	755(25)	479(20)	606(21)	-146(18)	104(18)	-32(16)
C(6b)	483(18)	473(19)	568(19)	-61(14)	83(15)	-6(15)
C(7)	639(22)	591(21)	684(23)	99(17)	54(18)	75(18)
C(8)	668(22)	651(21)	559(20)	-117(18)	264(17)	61(17)
C(9)	698(23)	739(24)	509(19)	-186(19)	108(17)	-42(17)
C(10)	759(24)	579(21)	765(25)	66(18)	411(21)	-16(18)
C(11)	588(20)	516(19)	614(20)	-133(16)	202(16)	-23(16)
C(12)	534(20)	521(20)	669(22)	48(15)	133(16)	92(16)

TABLE 3  
SIGNIFICANT BOND LENGTHS (Å) AND ANGLES (DEG) IN II (E.S.D.'S IN PARENTHESES)

P(1)—P(2)	2.204(1)	Si(3)—P(1)—P(2)	95.41(4)
P(2)—Si(1)	2.286(1)	P(1)—P(2)—Si(1)	95.86(4)
P(1)—Si(3)	2.268(1)	P(2)—Si(1)—Si(2)	100.6(1)
Si(1)—Si(2)	2.351(1)	Si(1)—Si(2)—Si(3)	100.8(1)
Si(2)—Si(3)	2.350(1)	Si(2)—Si(3)—P(1)	101.6(1)
Si(1)—C(7)	1.866(3)	C(7)—Si(1)—C(8)	109.8(2)
Si(1)—C(8)	1.865(3)	C(9)—Si(2)—C(10)	111.1(2)
Si(2)—C(9)	1.878(4)	C(11)—Si(3)—C(12)	110.0(2)
Si(2)—C(10)	1.878(4)	Si(3)—P(1)—C(1a)	101.0(1)
Si(3)—C(11)	1.867(3)	P(2)—P(1)—C(1a)	103.1(1)
Si(3)—C(12)	1.872(3)	P(1)—P(2)—C(1b)	101.5(1)
P(1)—C(1a)	1.849(3)	Si(1)—P(2)—C(1b)	103.1(1)
P(2)—C(1b)	1.844(3)		
C(1a)—C(2a)	1.374(4)		
C(2a)—C(3a)	1.389(5)		
C(3a)—C(4a)	1.370(5)		
C(4a)—C(5a)	1.359(5)		
C(5a)—C(6a)	1.392(4)		
C(1a)—C(6a)	1.382(4)		
C(1b)—C(2b)	1.381(4)		
C(2b)—C(3b)	1.379(5)		
C(3b)—C(4b)	1.360(5)		
C(4b)—C(5b)	1.354(5)		
C(5b)—C(6b)	1.375(5)		
C(1b)—C(6b)	1.382(4)		

polarization. The crystal was rather rectangular, with  $\mu$  3.44 cm<sup>-1</sup>, and the data were not corrected for absorption. Also there was no evidence of radiation damage during the data collection.

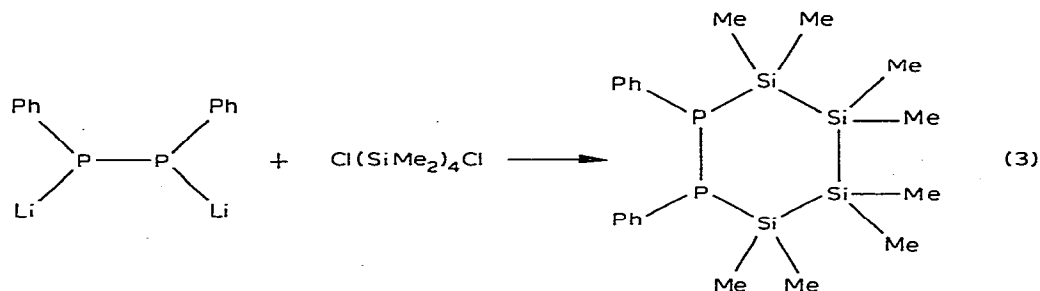
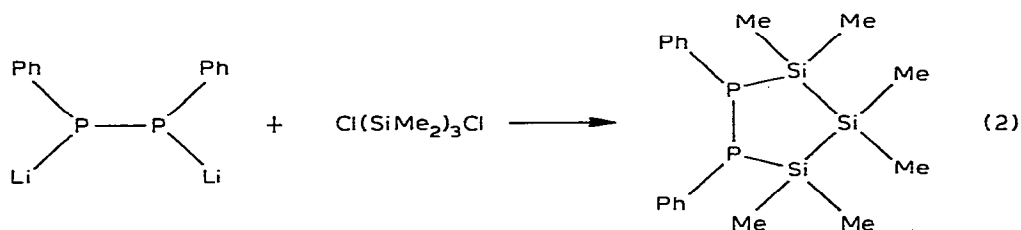
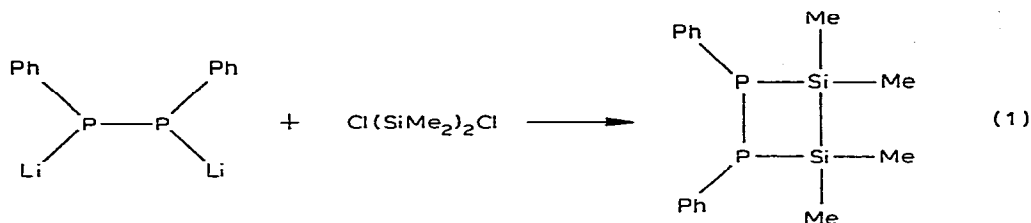
The structure was determined by direct methods and refined isotropically via block diagonal least squares to  $R_1 = 6.50$ ,  $R_2 = 9.00\%$ . Refinement was continued with anisotropic thermal parameters for all nonhydrogen atoms and converged to  $R_1 = 3.79$ ,  $R_2 = 5.09\%$ . A final full-matrix least squares cycle was performed on coordinates only to verify convergence and to calculate the variance-covariance matrix for error analysis. In the final cycle the average shift per error was 0.04. Final atomic parameters are given in Table 1. Anisotropic thermal parameters are given in Table 2. Bond lengths and angles are given in Table 3\*.

## Results

The reactions of 1,2-dilithium-1,2-diphenyldiphosphide with the 1,2-, 1,3- and 1,4-dichloropermethylopolysilanes Cl(SiMe<sub>2</sub>)<sub>n</sub>Cl ( $n = 2, 3, 4$ ) yield respectively four-, five- and six-membered heterocycles containing two adjacent phosphorus atoms (eqs. 1, 2 and 3). The four-membered ring is obtained in low yield with the principal product of reaction 1 being polymer [10]. Moderate yields of

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the five- and six-membered ring compounds are obtained from the ring closure reactions 2 and 3.



#### $^1\text{H}$ , $^{13}\text{C}$ , $^{31}\text{P}$ and $^{29}\text{Si}$ NMR of $(\text{PhP})_2(\text{SiMe}_2)_3$

Because  $(\text{PhP})_2(\text{SiMe}_2)_3$  has been fully characterized by  $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{31}\text{P}$  and  $^{29}\text{Si}$  NMR studies, the results for this compound will be described first. The  $^{31}\text{P}$ -decoupled  $^1\text{H}$  NMR spectrum of the silicon-methyl region at  $60^\circ\text{C}$  exhibits two singlets at 0.17 and 0.25 ppm in a ratio of 2 to 1 (Fig. 1). The  $^{31}\text{P}$ -coupled  $^1\text{H}$  NMR spectrum at the same temperature consists of a pseudotriplet at 0.18 ppm ( $J = 2.8$  Hz) and a singlet at 0.25 ppm (Fig. 2). When the temperature is lowered, the triplet resonance broadens and eventually disappears into the baseline near  $-16^\circ\text{C}$ . Upon further cooling this resonance reappears as two peaks. At the low temperature limit of  $-60^\circ\text{C}$  the  $^1\text{H}\{^{31}\text{P}\}$  NMR spectrum consists of three resonances of equal intensity at 0.40, 0.25 and  $-0.08$  ppm; in the uncoupled  $^1\text{H}$  spectrum the resonance at 0.40 is a pseudotriplet, that at 0.25 is a sharp singlet and the  $-0.08$  resonance is a broad peak (Figs. 1 and 2). \*

The temperature dependence of the proton NMR spectra is consistent with phosphorus inversion being slow on the NMR timescale at low temperatures but

\* The peak at 0.12 ppm in these spectra appears to be due to an impurity.

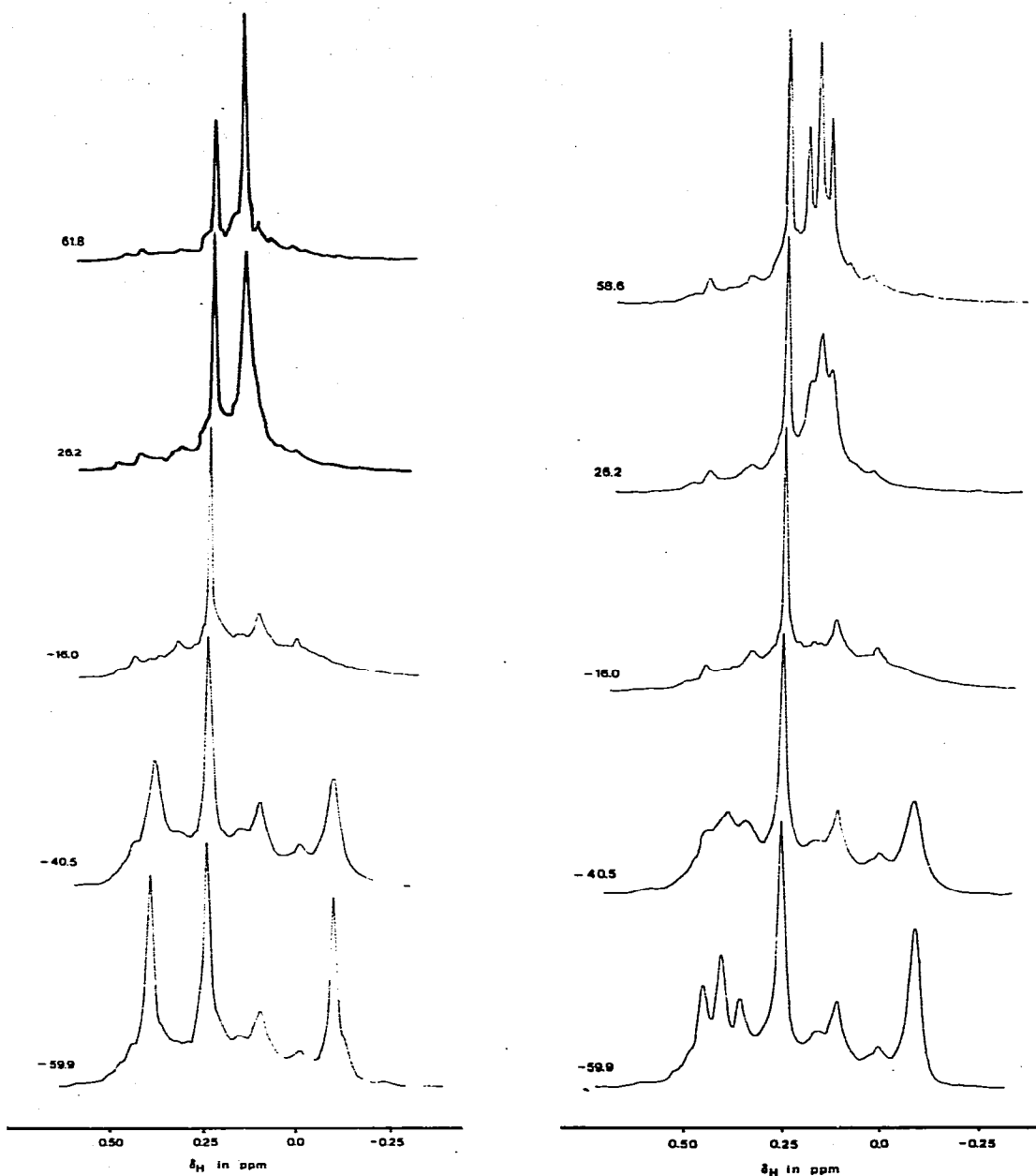


Fig. 1.  $^1\text{H}\{^{31}\text{P}\}$  NMR spectra of the silicon-methyl region of  $(\text{PhP})_2(\text{SiMe}_2)_3$  as a function of temperature ( $^\circ\text{C}$ ).

Fig. 2.  $^1\text{H}$  NMR spectra of the silicon-methyl region of  $(\text{PhP})_2(\text{SiMe}_2)_3$  as a function of temperature ( $^\circ\text{C}$ ).

becoming rapid at  $60^\circ\text{C}$ . The persistent singlet at 0.25 ppm is assigned to the two equivalent methyl groups on the unique silicon. The resonances at 0.40 and  $-0.08$  ppm at low temperature are assigned to the two pairs of geminal methyl groups adjacent to the phosphorus atoms, which are chemically inequivalent when phosphorus inversion is slow. The differing orientation of the methyl

groups relative to the phosphorus lone pairs probably accounts for the difference in the  $^{31}\text{P}$  coupling constants observed for these two resonances [11].

As the temperature is increased, phosphorus inversion results in chemical, but not magnetic, equivalence of the protons on the four methyl groups adjacent to phosphorus. The pseudotriplet observed for these protons at the high temperature limit is interpreted as resulting from deceptive simplicity of the X region of an  $\text{X}_6\text{AA}'\text{X}'_6$  spectrum in which the criterion  $|J(\text{AA}')| \gg |J(\text{AX}) - J(\text{AX}')|$  holds [12]. The observed coupling constant ( $J = 2.8$  Hz) is then the absolute value of the sum of the individual coupling constants,  $|J(\text{AX}) + J(\text{AX}')|$ .

The other NMR spectra for  $(\text{PhP})_2(\text{SiMe}_2)_3$  are all consistent with the assignments given above. The  $^{13}\text{C}\{^1\text{H}\}$  spectrum in the silicon-methyl region consists of two pseudotriplets at  $-3.09$  (4c,  $J = 7.7$  Hz) and  $-6.25$  ppm (2c,  $J = 2.3$  Hz). As in the  $^1\text{H}$  NMR spectra, the pseudotriplets are explained as resulting from deceptive simplicity of the X region of an  $\text{X}_6\text{AA}'\text{X}'_6$  spectrum in which  $|J(\text{AA}')| \gg |J(\text{AX}) - J(\text{AX}')|$ . In the  $^{31}\text{P}\{^1\text{H}\}$  spectrum a single resonance at  $-97.39$  ppm is observed at  $40^\circ\text{C}$  in perdeuterotoluene.

The  $^{29}\text{Si}\{^1\text{H}\}$  NMR spectrum exhibits two pseudotriplets at  $-12.47$  ppm ( $J = 12.0$  Hz) and  $-44.89$  ppm ( $J = 16.3$  Hz) (Fig. 3). Again a deceptively simple spectrum is observed. The signal at lower field is probably due to the silicon atoms adjacent to the more electronegative phosphorus atoms and consequently deshielded. In  $^{29}\text{Si}\{^1\text{H}\}$  NMR spectra obtained either at  $-13$  or  $-45^\circ\text{C}$ , the chemical shifts and coupling constants are identical with the values obtained at ambient temperature. The silicon atoms remain equivalent even when phosphorus inversion is slow, and so, as expected, the  $^{29}\text{Si}$  chemical shifts and coupling constants do not change with temperature.

#### $^1\text{H}$ , $^{13}\text{C}$ , $^{31}\text{P}$ and $^{29}\text{Si}$ NMR of $(\text{PhP})_2(\text{SiMe}_2)_4$

The NMR spectroscopic results obtained for  $(\text{PhP})_2(\text{SiMe}_2)_4$  are quite similar

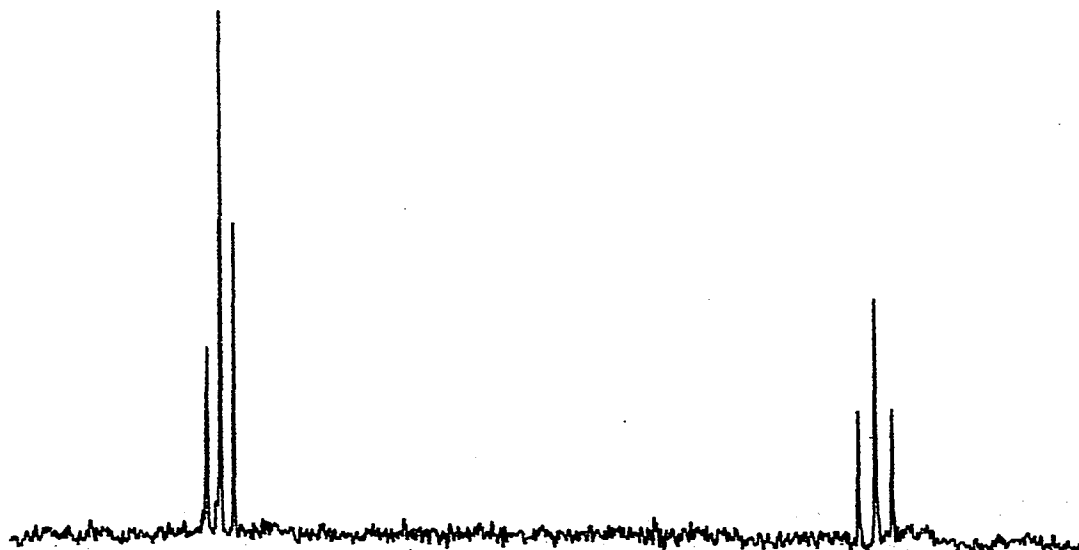


Fig. 3.  $^{29}\text{Si}\{^1\text{H}\}$  NMR spectrum of  $(\text{PhP})_2(\text{SiMe}_2)_3$ .



to those described above for  $(\text{PhP})_2(\text{SiMe}_2)_3$ . The  $^1\text{H}$  NMR spectrum at  $29^\circ\text{C}$  of the methyl-silicon region exhibits a pseudo-triplet at 0.14 ppm ( $J = 2.8$  Hz) and a singlet at 0.22 ppm. When phosphorus is decoupled, two single resonances of equal intensity are obtained at 0.14 ppm and 0.22 ppm. The 0.22 ppm singlet is unchanged at low temperatures and is therefore assigned to the methyl groups on the remote silicon atoms. The pseudotriplet can again be assigned as a deceptively simple  $X_6AA'X_6'$  pattern from the methyl groups on the silicon atoms adjacent to the phosphorus atoms. On lowering the temperature, this triplet broadens and disappears into the baseline at  $-18.5^\circ\text{C}$ . On further cooling two new resonances grow in. At  $-64^\circ\text{C}$  three resonances of approximately equal intensity are present in the  $^1\text{H}\{^{31}\text{P}\}$  NMR spectrum. The  $^1\text{H}$  NMR spectrum at the same temperature exhibits a pseudotriplet at 0.35 ppm ( $J = 4.6$  Hz), a singlet at 0.22 ppm and a broad resonance at  $-0.12$  ppm. The  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of the silicon-methyl region consists of two pseudotriplets at 1.91 ppm ( $J = 7.69$  Hz) and  $-1.20$  ppm ( $J = 2.32$  Hz) (Fig. 4). One resonance at  $-97.96$  ppm is present in the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum at ambient temperature. In the  $^{29}\text{Si}\{^1\text{H}\}$  spectrum two pseudotriplets are observed at  $-12.52$  ppm ( $J = 13.0$  Hz) and  $-44.39$  ppm ( $J = 16.2$  Hz).

#### $^1\text{H}$ NMR of $(\text{PhP})_2(\text{SiMe}_2)_2$

The  $^1\text{H}$  NMR spectrum of the four-membered ring,  $(\text{PhP})_2(\text{SiMe}_2)_2$ , in the silicon-methyl region exhibits a complex non-first order pattern at ambient temperature. Evidently the geminal methyl groups are chemically inequivalent and the chemical shift difference between the pairs of inequivalent methyl groups is small enough that the resonances overlap. On warming to  $87^\circ\text{C}$  the  $^1\text{H}$  NMR spectrum of the silicon-methyl region of  $(\text{PhP})_2(\text{SiMe}_2)_2$  simplifies to a pseudotriplet at 0.17 ppm ( $J = 2.8$  Hz). At this temperature the four methyl groups are chemically equivalent due to rapid phosphorus inversion and their resonance appears as a pseudotriplet corresponding to the X region of an  $X_6AA'X_6'$  spectrum.

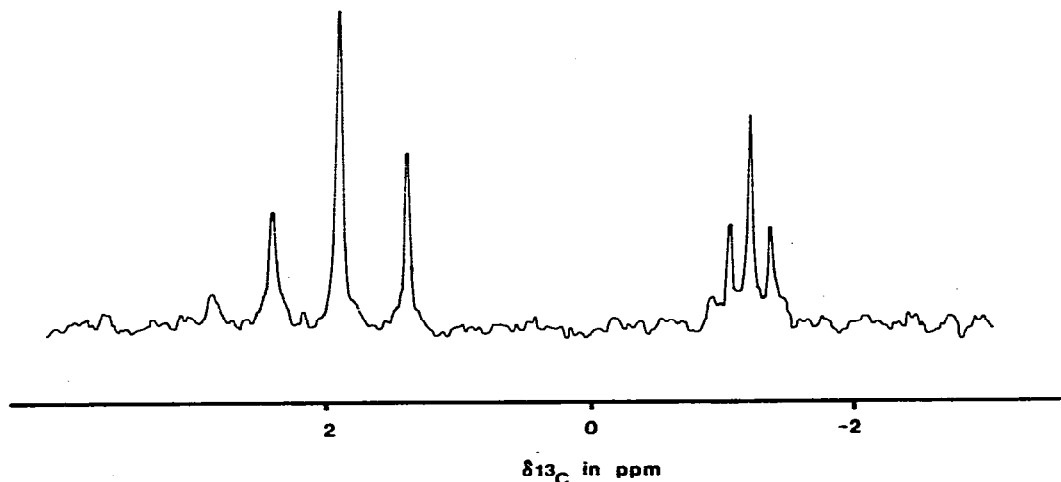


Fig. 4.  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of the silicon-methyl region of  $(\text{PhP})_2(\text{SiMe}_2)_4$ .

## Discussion

The results of the nuclear magnetic resonance studies on the diphosphacyclosilanes are summarized in Tables 4 and 5. All of the results are consistent with phosphorus inversion, occurring slowly at low temperatures but rapidly on the NMR timescale at some higher temperatures. Inversion at phosphorus interconverts the *meso* and *dl* diastereomeric forms of these compounds and equilibrates the four methyl groups on the two silicon atoms adjacent to the phosphorus atoms. One form must predominate at low temperature because only two resonances are observed for these chemically inequivalent methyl groups in the  $^1\text{H}$  NMR spectra at low temperature. Coalescence temperatures and  $\Delta G^\ddagger$  values are listed in Table 6. The similar values for  $(\text{PhP})_2(\text{SiMe}_2)_3$  and  $(\text{PhP})_2(\text{SiMe}_2)_4$  indicate that the barrier to phosphorus inversion changes very little between the five- and six-membered rings.

In the smaller four-membered ring,  $(\text{PhP})_2(\text{SiMe}_2)_2$ , angle strain is increased in the transition state for phosphorus inversion. This effect raises the barrier to phosphorus inversion relative to the five- and six-membered heterocycles, and leads to a complex  $^1\text{H}$  NMR spectrum for the four-membered ring species at ambient temperature. At  $87^\circ\text{C}$  the  $^1\text{H}$  NMR spectrum of the silicon-methyl region of  $(\text{PhP})_2(\text{SiMe}_2)_2$  simplified to a pseudotriplet. The four methyl groups become chemically equivalent at high temperature as a result of rapid phosphorus inversion. A  $\Delta G^\ddagger$  value of 15.2 kcal/mol for phosphorus inversion was estimated from the width of the low temperature spectrum and the approximate coalescence temperature of  $34^\circ\text{C}$  \*. The free energy of activation for phosphorus inversion in  $(\text{PhP})_2(\text{SiMe}_2)_2$  is about 2.5 kcal/mol higher than that found for the corresponding five-membered ring. Interestingly in cyclic amines the strain effect of a four-membered ring amounts to approximately 1–2 kcal/mol relative to the analogous five-membered ring system [13]. Our results, although approximate for the four-membered phosphasilane, would seem consistent.

In Table 7  $\Delta G^\ddagger$  data for phosphorus inversion in  $(\text{PhP})_2(\text{SiMe}_2)_3$ ,  $(\text{PhP})_2(\text{SiMe}_2)_4$  and related compounds are presented. The barrier to phosphorus inversion in the sila- and disilaphospholanes is significantly lower than in phosphacyclopentanes. As Mislow and his group originally pointed out, the decrease in inversion barrier going from alkylphosphines to silylphosphines can be explained on the basis of the lower electronegativity of silicon than carbon [15–17]. The free energies of activation for phosphorus inversion in  $(\text{PhP})_2(\text{SiMe}_2)_3$  and  $(\text{PhP})_2(\text{SiMe}_2)_4$  are quite similar to that for the disilaphospholane. The low values are reasonable for the cyclic disila-substituted diphosphines, for which angle strain in the transition state is minimal.

### Crystal structure of $(\text{PhP})_2(\text{SiMe}_2)_3$ (II)

An ORTEP drawing which shows a general view of the molecule and gives the crystallographic numbering scheme is presented in Fig. 5. At least in the crystalline state, molecules of  $(\text{PhP})_2(\text{SiMe}_2)_3$  exist in the *trans* form. In this

\* The difference in  $\Delta G^\ddagger$  for pyramidal inversion in five- and six-membered ring phosphacycloalkanes is also small, although the magnitudes of  $\Delta G^\ddagger$  for these compounds are much greater than for the diphosphacyclosilanes (Table 7).

TABLE 4

<sup>1</sup>H NMR PARAMETERS OF THE DIPHOSPHACYCLOPOLYSILANES (PhP)<sub>2</sub>(SiMe<sub>2</sub>)<sub>n</sub>

Compound	Temp (°C)	SiMe <sub>2</sub> group <sup>a</sup>	<sup>1</sup> H <sup>b</sup>
(PhP) <sub>2</sub> (SiMe <sub>2</sub> ) <sub>4</sub>	29.0	α	0.14(t, 2.8)
		β	0.22
	-63.8	α	-0.12(broad)
		β	0.22
(PhP) <sub>2</sub> (SiMe <sub>2</sub> ) <sub>3</sub>	58.6	α	0.18(t, 2.8)
		β	0.25
	-59.9	α	-0.08(broad)
		β	0.25
(PhP) <sub>2</sub> (SiMe <sub>2</sub> ) <sub>2</sub>	86.9	α'	0.40(t, 4.6)
		α	0.17(t, 2.8)
		α	0.17(t, 2.8)

<sup>a</sup> SiMe<sub>2</sub> groups are lettered alphabetically from the phosphorus atoms. <sup>b</sup> δ (in ppm) in CDCl<sub>3</sub> solution, reference internal TMS. Phenyl region not included. *J*(PH) (in parentheses) are reported in Hertz.

conformation, with the phenyl groups in pseudoequatorial positions, lone-pair—lone-pair repulsion is minimized. The five-membered P<sub>2</sub>Si<sub>3</sub> ring is quite puckered as indicated by the large ring torsional angles shown in Table 8. The observed sequence of torsional angles is indicative of a twisted conformation with a two-fold symmetry axis [17]. The angle between the line of the phosphorus—phosphorus bond and the plane formed by the three silicon atoms is 42.9°. In contrast, the five-membered rings in (PhP)<sub>5</sub> [21] and Si<sub>5</sub>Me<sub>9</sub>SiMe<sub>2</sub>[Fe(CO)<sub>2</sub>(C<sub>5</sub>H<sub>5</sub>)] [22] adopt envelope structures with one ring torsional angle of about 0°.

In conjunction with the twisted conformation of the five-membered ring, the cross-ring distances are all well within their respective Van der Waals' distances (3.90 and 4.20 Å for P—Si and Si—Si distances, respectively). These distances are presented in Table 9 together with the cross-ring, non-adjacent, P—P distances in (PPh)<sub>5</sub> for comparison. The P(1)—Si(1) and P(2)—Si(3) distances are the shortest cross-ring interactions in (PhP)<sub>2</sub>(SiMe<sub>2</sub>)<sub>3</sub> and in relative terms these distances are shorter than any of the non-adjacent P—P distances in (PPh)<sub>5</sub>.

TABLE 5

<sup>13</sup>C, <sup>31</sup>P AND <sup>29</sup>Si NMR PARAMETERS OF THE DIPHOSPHACYCLOPOLYSILANES (PhP)<sub>2</sub>(SiMe<sub>2</sub>)<sub>n</sub>

Compound	<sup>31</sup> P{ <sup>1</sup> H} <sup>a</sup>	SiMe <sub>2</sub> group <sup>b</sup>	<sup>13</sup> C{ <sup>1</sup> H} <sup>c</sup>	<sup>29</sup> Si{ <sup>1</sup> H} <sup>c</sup>
(PhP) <sub>2</sub> (SiMe <sub>2</sub> ) <sub>4</sub>	-97.96	α	1.91(t, 7.69)	-12.52(t, 13.00)
		β	-1.20(t, 2.32)	-44.39(t, 16.20)
(PhP) <sub>2</sub> (SiMe <sub>2</sub> ) <sub>3</sub>	-97.39	α	-3.09(t, 7.69)	-12.47(t, 12.00)
		β	-6.25(t, 2.26)	-44.89(t, 16.25)

<sup>a</sup> δ (in ppm), in CDCl<sub>3</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 atoms. <sup>c</sup> δ (in ppm), in C<sub>6</sub>D<sub>6</sub> solution, references C<sub>6</sub>D<sub>6</sub> and TMS. Phenyl region not included in <sup>13</sup>C spectra. *J*(PC) and *J*(PSi) (in parentheses) are reported in Hertz.

TABLE 6

FREE ENERGY OF ACTIVATION AND SPECTRAL PARAMETERS FOR PHOSPHORUS INVERSION IN  $(\text{PhP})_2(\text{SiMe}_2)_n$

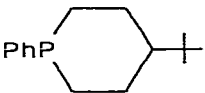
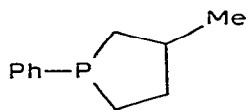
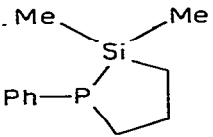
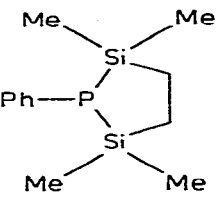
Compound	$T_c$ ( $^\circ\text{C}$ ) <sup>a</sup>	$\Delta\nu$ (Hz at 100 MHz)	$\Delta G^\ddagger$ (kcal/mol)
$(\text{PhP})_2(\text{SiMe}_2)_3$	-16.0	48.0	12.6
$(\text{PhP})_2(\text{SiMe}_2)_4$	-18.5	47.0	12.4
$(\text{PhP})_2(\text{SiMe}_2)_2$	~34	~40	~15.2

<sup>a</sup> Coalescence temperature.

The cross-ring interactions P(1)—Si(1) and P(2)—Si(3) are also much shorter than analogous P—Si distances in  $(\text{PhPSi}_2\text{Me}_4)_2$  (3.641 and 3.654 Å) [23]. Several factors undoubtedly influence the twisted structure of  $(\text{PhP})_2(\text{SiMe}_2)_3$ , but it is possible that non-adjacent phosphorus—silicon interactions may contribute to this conformation.

TABLE 7

SELECTED VALUES OF FREE ENERGY OF ACTIVATION FOR PHOSPHORUS INVERSION

Compound	$\Delta G^\ddagger$ (kcal/mol)	Ref.
	35.2	14
	36	15
	21.3	18
	13.2	19
$(\text{PhP})_2(\text{SiMe}_2)_3$	12.6	This work
$(\text{PhP})_2(\text{SiMe}_2)_4$	12.4	This work

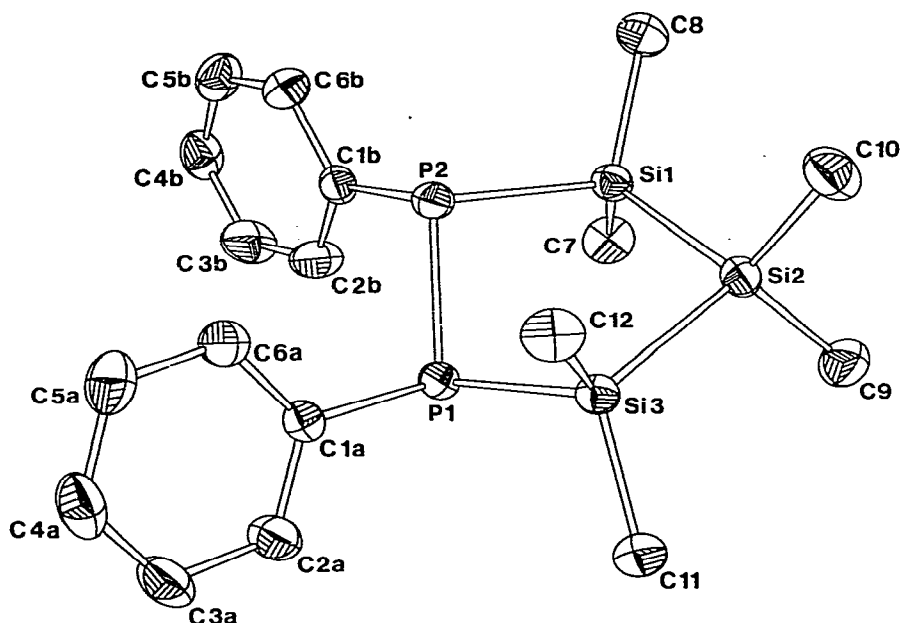


Fig. 5. An ORTEP drawing of  $(\text{PhP})_2(\text{SiMe}_2)_3$  showing the atom labels. Thermal ellipsoids are drawn at the 30% probability level.

The two silicon–silicon distances are equivalent (2.350 Å) and are similar to the values observed in  $(\text{PhPSi}_2\text{Me}_4)_2$  (2.345 Å) [23],  $(\text{OSi}_2\text{Me}_4)_2$  (2.35 Å) [24] and  $(\text{Me}_2\text{Si})_6$  (2.338 Å) [25]. The phosphorus–silicon distances (2.287 and 2.268 Å) are rather long but are within the range of values previously reported. Similar distances are observed for  $\text{P}_4(\text{SiMe}_2)_3$  (2.283, 2.247 Å) [26], in which the phosphorus and silicon atoms are incorporated into five-membered rings. The phosphorus–phosphorus distance (2.204 Å) is also similar to that found in  $\text{P}_4(\text{SiMe}_2)_3$  (2.202 Å) [26]  $\text{P}_7(\text{SiMe}_3)_3$  (2.180, 2.192, 2.214 Å) [23] and  $(\text{PPh})_5$  (2.217 Å) [21].

The ring angles at the phosphorus atoms, 95.38 and 95.85°, are significantly smaller than the ring angles at the silicon atoms, 100.60, 100.78, 101.61°. The endocyclic angles in  $(\text{PPh})_5$  [21] vary from 94.05 to 107.24° while in  $(\text{PPh})_6$  [27] these angles are all close to the average of 95.52°. Apparently, phosphorus accepts small endocyclic angles better than silicon. This trend can be rationalized in terms of exocyclic lone pair–bond pair repulsions in the phosphorus

TABLE 8

TORSIONAL ANGLES FOR II (DEG.)

Line 1	Line 2	Angle
P(2) P(1)	Si(1) Si(2)	-55.917
P(2) Si(1)	Si(3) Si(2)	29.232
Si(1) Si(2)	P(1) Si(3)	29.431
Si(2) Si(3)	P(2) P(1)	-55.436
Si(3) P(1)	Si(1) P(2)	66.807

TABLE 9  
CROSS-RING DISTANCES FOR (PhP)<sub>2</sub>(SiMe<sub>2</sub>)<sub>3</sub> AND (PhP)<sub>5</sub>

(PhP) <sub>2</sub> (SiMe <sub>2</sub> ) <sub>3</sub>			(PhP) <sub>5</sub>		
Atom 1	Atom 2	Distance (Å)	Atom 1	Atom 2	Distance (Å)
P(1)	Si(1)	3.334	P(1)	P(3)	3.57
P(2)	Si(3)	3.308	P(2)	P(4)	3.24
P(1)	Si(2)	3.580	P(3)	P(5)	3.40
P(2)	Si(2)	3.568	P(4)	P(1)	3.27
Si(1)	Si(3)	3.622	P(5)	P(2)	3.49

being larger than the corresponding bond pair—bond pair repulsions in the silicon compounds.

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