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CYCLIC POLYSILANES

XIII *. RING CLOSURE REACTIONS OF α,ω-DICHLOROPERMETHYLPOLYSILANES; THE PREPARATION OF HETEROCYCLIC PHENYLPHOSPHAPERMETHYLSILANES $(PhP)_m(SiMe_2)_n$

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Summary

The reactions of the dichloropermethylsilanes $Cl(SiMe_2)_nCl$ (n = 1—6) with dilithium phenylphosphide yield a series of novel heterocyclic phosphasilanes. For n = 4, 5 and 6, the reaction leads to the corresponding 5-, 6- and 7-membered cyclic monophosphapolysilanes $PhP(SiMe_2)_n$, but when n = 3, a polymeric material of probable formula $[PhP(SiMe_2)_3]_n$ is formed. For n = 2, ring closure again occurs, to yield the 6-membered P_2Si_4 ring compound $[PhP(SiMe_2)_2]_2$. With dimethyldichlorosilane, cyclization results in the dimeric phosphasilane $(PhPSiMe_2)_2$ at —40°C, and the corresponding trimeric derivative $(PhPSiMe_2)_3$ at +40°C. These two ring sizes exist in an equilibrium $(PhPSiMe_2)_2 \rightleftharpoons (PhPSiMe_2)_3$, the dimer being stable at room temperature, but being converted into the trimer above 150°C. The ^1H, ^{13}C, ^{29}Si and ^{31}P NMR parameters are reported for all the compounds, and the chemical shifts and coupling constants interpreted in terms of the molecular and electronic structures of the different ring sizes.

Introduction

One of the more common methods for the preparation of heterocyclic polysilanes involves the ring closure reaction of an α,ω-dihalopolysilane with an appropriate heteroatom compound. Until now, however, most reactions have used only the dichlorosilanes or 1,2-dichlorodisilanes. A convenient preparation of the longer chain α,ω-dichloropermethylpolysilanes $Cl(SiMe_2)_nCl$ (n = 2—6) by the direct chlorination of $(SiMe_2)_{5,6}$ has recently been described [2,3], and

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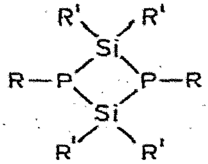
* For part XII see ref. 1.

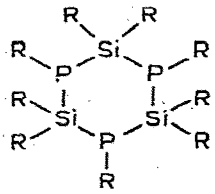
the consequent ready availability of the entire series of dichlorosilanes $Cl(SiMe_2)_n$-Cl (n = 1—6) has prompted us to carry out a study of their usefulness as reagents for the synthesis of heterocyclic polysilanes. We have begun by examining the reactions of the α,ω-dichloropermethylsilanes $Cl(SiMe_2)_nCl$ (n = 1—6) with dilithium phenylphosphide to give a series of heterocyclic phosphasilane derivatives.

In contrast to the wide variety of silicon—nitrogen heterocycles known, there have been relatively few reports concerning the preparation of cyclic molecules containing a silicon—phosphorus skeleton. The first paper to deal with such compounds (as well as later papers) described a number of ring and cage molecules based on the alternating 4-membered P_2Si_2 ring I [4—6], and subsequent work indicated that a 6-membered P_3Si_3 ring II was also possible [5] *.



(I)

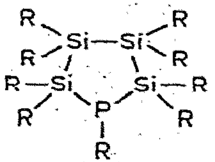
(R = Ph, H; R' = Et; R = R' = Ph;
R = SiMe$_3$; R' = Me)



(II)

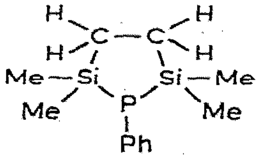
(R = Ph)

Polysilane heterocycles containing a single phosphorus atom are also known. The 5-membered phosphatetrasilane ring III has been prepared by the reaction of the 1,4-dilithio derivative $Li(SiPh_2)_4Li$ with phenyldichlorophosphine [7] and more recently the preparation of the phosphadicarbadisilane IV has been described [8].



(III)

(R = Ph)



(IV)

Results and discussion

The reactions of the 1,4-, 1,5- and 1,6-dichloropermethylpolysilanes $Cl(SiMe_2)_n$-Cl (n = 4, 5, 6) with dilithium phenylphosphide yield respectively 5-, 6- and 7-membered heterocycles containing one phosphorus atom (eq. 1 **). The yields of these reactions, which were carried out in tetrahydrofuran solution at room

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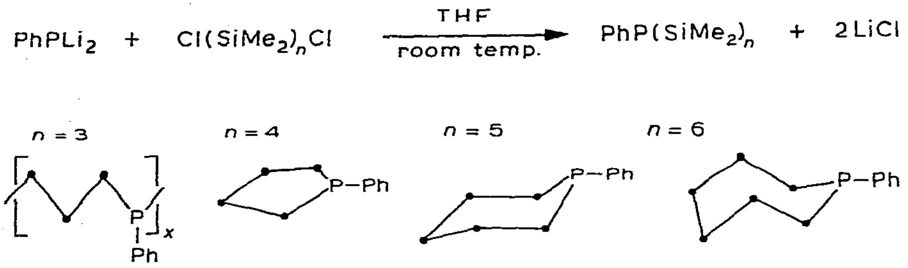
* A review [6a] mentions an unpublished preparation of the four-membered ring $PhPPhPSiMe_2SiMe_2$ from $(Me_2SiCl)_2$ and $(PhPK)_2$, but from our investigation of this reaction (to be reported later) we believe it doubtful that this compound was obtained.

** Here and elsewhere in this paper the notation ⋏ will be used to denote the $SiMe_2$ moiety. PPh groups are all shown in equatorial positions. This assumption is shown to be correct by a recent crystal structure of P_2Si_4 [9].

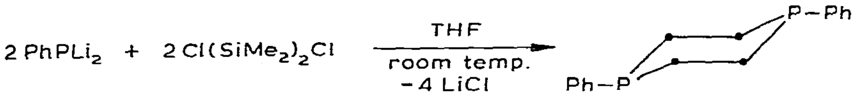


(1)

temperature, ranged from 66—82%, suggesting that competing side reactions such as polymerizations are relatively unimportant. This is not the case however in the reaction involving the dichlorotrisilane $Cl(SiMe_2)_3Cl$, which gives neither a 4-membered ring containing one phosphorus atom, nor an 8-membered ring containing two phosphorus atoms. Instead an uncharacterized insoluble polymer, presumably of formula $[PhP(SiMe_2)_3]_x$, is formed (eq. 1). Evidently the 4-membered ring is too strained to close, and the 8-membered ring is too sterically crowded.

These results are similar to those obtained from the condensation of dichlorodimethylsilane with sodium—potassium alloy, which produces the 6-membered ring as the principal product along with smaller amounts of the 5- and 7-membered cyclosilanes [10]. The tetrameric and octameric derivatives $(Me_2Si)_{4,8}$ have not been isolated from this type of reaction. Moreover, the condensation of α,ω-dichloropolysilanes $Cl(SiMe_2)_nCl$ ($n = 4, 5, 6$) with alkali metals produces the expected $(Me_2Si)_n$ rings for $n = 5$ and 6, but only polymer (and some $(Me_2Si)_6$) for $n = 4$ [11]. It is apparent that the cyclization of dichloropolysilanes $Cl(SiMe_2)_nCl$ in polar reactions is favorable only when a 5-, 6- or 7-membered ring can be formed. Because of the angle strain or steric bulk associated with smaller and larger rings, polymerization is favored over ring closure when their preparation is attempted.

Consistently with this conclusion the reaction of the 1,2-dichlorodisilane ($Cl(SiMe_2)_2Cl$) with dilithium phenylphosphide yields the novel 6-membered P_2Si_4 ring compound $[PhP(SiMe_2)_2]_2$ (eq. 2). Similar results have been obtained



(2)

from the hydrolysis of $Cl(SiMe_2)_2Cl$ [12], and from its reaction with primary amines [13] and hydrogen sulphide [14]. These reactions all proceed to yield a 6-membered E_2Si_4 ring (E = O, N, S).

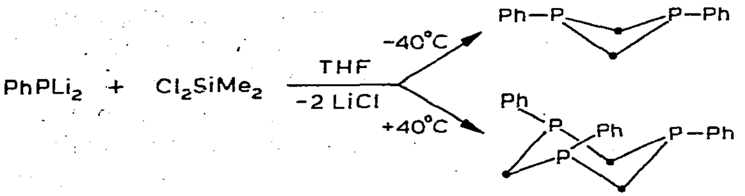
The reaction of dichlorodimethylsilane with $PhPLi_2$ is unusual in that two different cyclic products are obtained depending on the reaction conditions. At —40°C, ring closure of dilithium phenylphosphide with dichlorodimethylsilane results in the formation of the 4-membered P_2Si_2 ring (eq. 3a), but when the same reaction is carried out at ambient temperature, the 6-membered P_3Si_3 ring is produced (eq. 3b).

TABLE 1

^{31}P ^{a}, ^{1}H ^{b}, ^{13}C ^{b} AND ^{29}Si ^{b} NMR PARAMETERS OF THE PHOSPHASILANES $(PhP)_n(SiMe_2)_m$

Compound	$^{31}P\{^1H\}$	$SiMe_2$ group ^{c}	^1H	$^{13}C\{^1H\}$	$^{29}Si\{^1H\}$
$PhP(SiMe_2)_6$	−140.5	α	0.31(~5.0) ^{d}	−0.82(5.98)	−16.89(52.50)
		β	0.28	−5.30(4.76)	−42.83(33.74)
		γ	0.25	−5.29(1.83)	−42.11(0.9)
$PhP(SiMe_2)_5$	−138.0	α	0.34(5.0)	−1.33(8.42)	−17.48(48.00)
		β	0.27	−5.98(4.52)	−43.01(27.50)
		γ	0.28	−5.85(1.10)	−42.41(3.5)
$PhP(SiMe_2)_4$	−132.8	α	0.36(6.8)	−1.59(12.94)	−11.91(39.27)
		β	0.23	−5.92(2.13)	−42.60(12.00)
$[PhP(SiMe_2)_2]_2$	−139.4		0.43	−1.38	−18.99
			(^3J 4.9, ^4J 0.9) ^{e}	($^2J = {}^3J = 6.22$) ^{e}	(^1J 46.37, ^2J 24.62)
$[PhPSiMe_2]_3$	−135.3		0.56	+2.56	−0.14
			(^3J 3.3, ^5J 3.2)	(^2J 12.33, ^4J 1.47) ^{e}	(^1J 40.00, ^3J 1.88) ^{e}
$[PhPSiMe_2]_2$	−123.3		0.49(4.2)	+2.64(12.36)	−1.07(26.74)
$PhP(SiMe_2SiMe_3)_2$	−124.7	α	0.42(5.5)	−1.28(9.52)	−17.30(52.80)
		β ^{f}	0.05	−1.78(2.20)	−15.59(20.00)

[a] δ (in ppm), in C_6D_6 solution, reference external H_3PO_4. Chemical shifts upfield of H_3PO_4 have a negative sign. [b] δ (in ppm), in C_6D_6 solution, reference internal TMS. Phenyl region not included in ^{1}H and ^{13}C spectra. J(PH), J(PC) and J(PSi) (in parentheses) are reported in Hertz. [c] $SiMe_2$ groups are lettered alphabetically from the phosphorus atom. [d] Signal partly obscured by other peaks, coupling constant is approximate. [e] Non-first order coupling pattern, see text for details. [f] $SiMe_3$ group.



(3a)

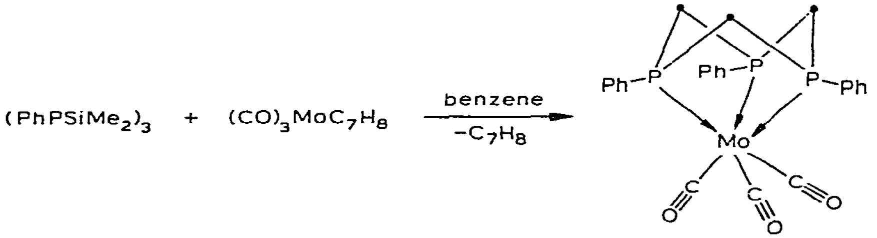
(3b)

The marked effect of temperature on this reaction emphasizes the delicate balance that must exist between the mechanisms of ring closure and chain propagation, the former being favored by lower temperatures. The formation of the 4-membered ring in this reaction, but not in that involving the 1,3-dichlorotrisilane (eq. 1), can be attributed to the greater ability of phosphorus to accept a small (less than tetrahedral) ring angle.

Like the cyclic dimethylsilathianes $(Me_2SiS)_{2,3}$, which are known to exist in an equilibrium between the dimeric and trimeric forms [15—17], the phosphasilanes $(PhPSiMe_2)_{2,3}$ also appear to interconvert. Preliminary experiments suggest that, in contrast to the silathiane system, the 4-membered phosphasilane ring is stable at room temperature indefinitely, and in solution the trimer is partially converted to it upon standing. At 150°C, the equilibrium favors the larger ring size, samples of the dimer being transformed almost exclusively into the trimer after several days at this temperature (eq. 4).

$$(PhPSiMe_2)_2 \overset{150^\circ C}{\rightleftharpoons} (PhPSiMe_2)_3 \qquad (4)$$

The dimeric and trimeric forms are most easily separated by fractional distillation in vacuo. The dimer is a crystalline solid but because the trimer is a viscous gum at room temperature, it is more difficult to handle. Complete characterization of this molecule was achieved through the formation of its molybdenum tricarbonyl complex $(PhSiMe_2)_3Mo(CO)_3$, which, like its perphenylated analog $(PhPSiPh_2)_3Mo(CO)_3$ [5], is expected to have the tridentate chelate structure shown in eq. 5.



(5)

^1H, ^{13}C, ^{29}Si and ^{31}P NMR spectra

The ^1H, ^{13}C, ^{29}Si and ^{31}P NMR parameters of the phosphorus—silicon heterocycles prepared in this work are given in Table 1 *. As the structural formulas shown in eq. 1 suggest, any conformational rigidity of the 5-, 6- and 7-membered

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* For purposes of comparison, the NMR spectra of the acyclic silylphosphine $PhP(SiMe_2SiMe_3)_2$ have also been recorded. This compound was prepared by the reaction of dilithium phenylphosphide with $Me_3SiSiMe_2Cl$ (see experimental section for details).

rings $PhP(SiMe_2)_{4,5,6}$ will produce an inequivalence in the two methyl groups bound to the same silicon atom. However, the single ^1H and ^{13}C resonances observed for all the geminal methyl groups in these molecules indicate that at room temperature conformational equilibration is rapid. Moreover, in contrast to recent work on the phosphorinane V (T_c −80°C) [18] and the phosphadicarbadisilane IV (T_c −17°C) [8], low temperature (>−100°C) ^{31}P NMR spectroscopy failed to reveal any conformational isomers.

(V)

The more symmetrical molecules show some interesting non-first order coupling patterns. The 6-membered P_2Si_4 ring compound can exist in a variety of different conformations, with the phenyl groups occupying axial or equatorial positions, but as before, only averaged signals are observed at ambient temperatures for the geminal methyl groups in both the ^1H and ^{13}C NMR spectrum of $[PhP(SiMe_2)_2]_2$. The ^1H resonance appears (Fig. 1) as a pair of partially overlapping doublets, the inner one being less well resolved than the outer. Such a spectrum is consistent with the pattern expected for an AX_{12}-$X'_{12}A'$ spin system, in which $J_{AA'} << |J_{AX} - J'_{AX}|$ [19,20]. On this basis, the separation of the outer doublet (5.8 Hz) corresponds to $|^3J(PH) + {}^4J(PH)|$ and that of the inner doublet (4.0 Hz) to $|^3J(PH) - {}^4J(PH)|$. Assuming that $^3J(PH)$ and $^4J(PH)$ are both positive (the former generally is) [21], the two coupling constants can be assigned the values $^3J(PH)$ 4.9 Hz and $^4J(PH)$ 0.9 Hz. The ^{13}C resonance of $[PhP(SiMe_2)_2]_2$ shows a triplet, the expected ABX pattern being

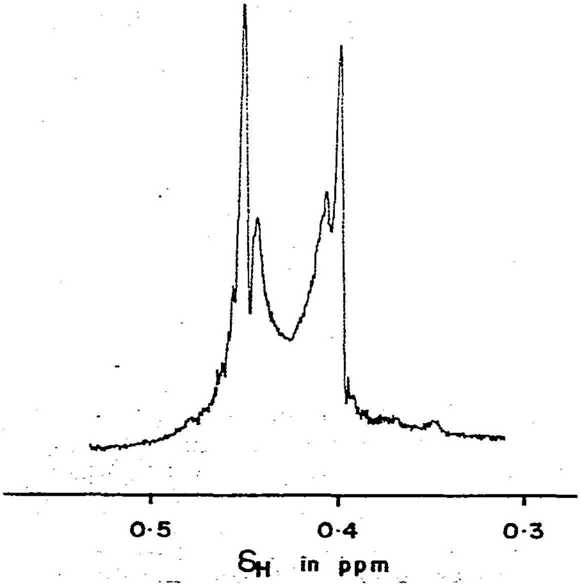

Fig. 1. 100 MHz ^1H NMR spectrum of $[PhP(SiMe_2)_2]_2$.

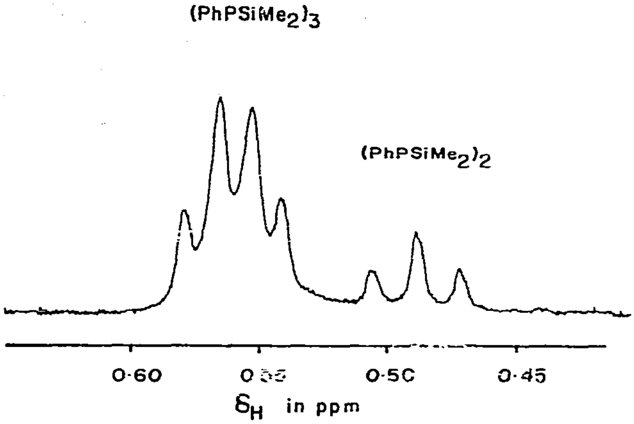

Fig. 2. 270 MHz ^{1}H NMR spectrum of a mixture of (PhPSiMe$_2$)$_2$ and (PhPSiMe$_2$)$_3$.

simplified by the near equivalence of J_{AX} and J_{BX}. The ^{29}Si spectrum gives rise to a normal first order pattern, the single resonance being split into a doublet of doublets by the two magnetically inequivalent phosphorus nuclei.

The ^{1}H, ^{13}C and ^{29}Si NMR spectra of the 4- and 6-membered alternating phosphorus—silicon rings [PhPSiMe$_2$]$_{2,3}$ are quite different. For the dimeric compound, simple triplet patterns are found for the resonances of all three nuclei (e.g. Figs. 2 and 3). The spectra of the trimer are more complex. The proton resonance (Fig. 2) appears as a doublet of triplets, the values of ^3J(PH) and ^5J(PH) being almost equivalent. The ^{13}C and ^{29}Si NMR spectra both give rise to AB$_2$X coupling patterns [22,23]; the observed ^{13}C NMR spectrum along with a computer simulation of it is shown in Fig. 3.

The variations in the coupling constants J(PX) (X = H, C, Si) as a function of ring size are of particular interest. The dependence is most marked for ^1J(PSi) and ^2J(PSi) (Fig. 4), both values increasing steadily with ring size. Although little is known about the factors affecting P—C and P—Si coupling constants, if it is assumed that a Fermi contact interaction provides the major contribution to the coupling constants [24—26], then the observed changes in ^1J(PSi) and ^2J(PSi) provide a useful measure of the *s*-character of the ring bonds in the (PhP)$_m$(SiMe$_2$)$_n$ molecules. Consequently the larger values of ^1J(PSi) and ^2J(PSi) observed for the larger P$_m$Si$_n$ rings can be interpreted as the result of the wider endocyclic bond angles found in them. In the molecules containing more than one phosphorus atom, the ring angles are expected to be smaller than in the PhP(SiMe$_2$)$_{4,5,6}$ series. Consistently, the ^1J(PSi) values of (PhPSiMe$_2$)$_{2,3}$ and [PhP(SiMe$_2$)$_2$]$_2$, and the ^2J(PSi) value of [PhP(SiMe$_2$)$_2$]$_2$ are lower than the corresponding values in the monophosphapolysilanes. When there are no cyclic constrictions on the size of the bond angle at silicon, as in PhP(SiMe$_2$SiMe$_3$)$_2$, ^1J(PSi) has an expectedly large value (52.80 Hz) *.

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* Further substantiation of this interpretation comes from the values of ^1J(FSi) and ^2J(FSi) for the series of linear α,ω-difluoropermethylpolysilanes F(SiMe$_2$)$_n$F (n = 2—6), which remain almost constant with change in chain length. In these compounds cyclic constraints are absent, and variations in bond angles, and hence σ-hybridization, as a function of chain length are not expected to occur [27].

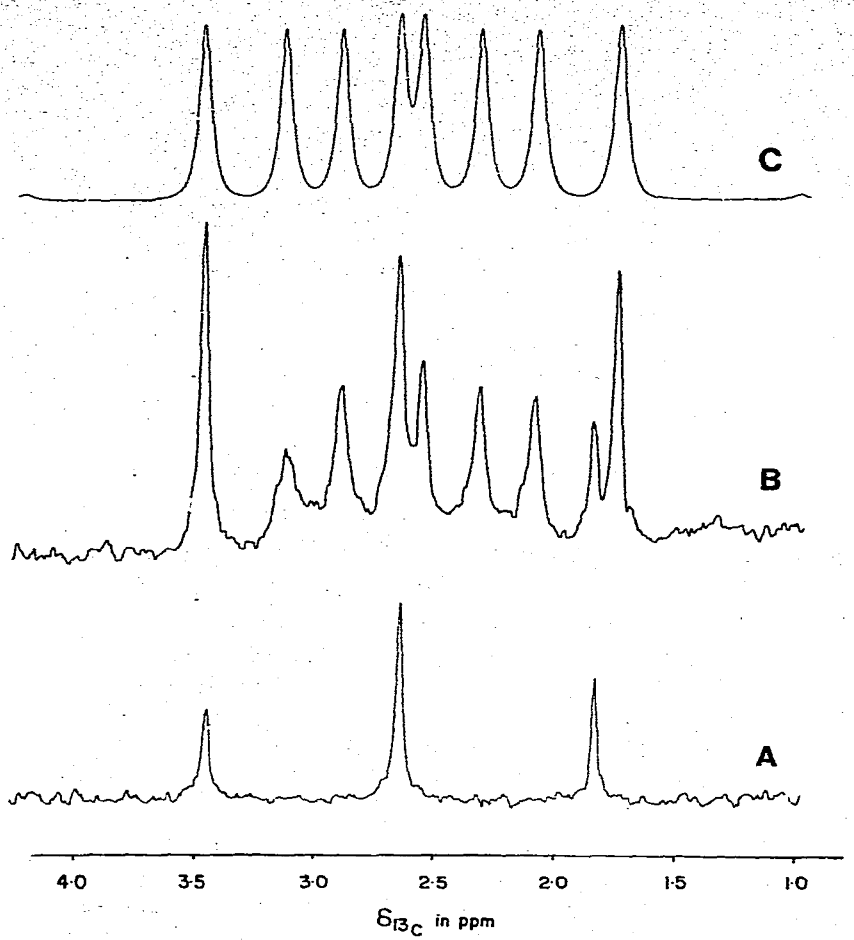


Fig. 3. The observed ^{13}C NMR spectrum (at 14.05 MHz) of $(PhPSiMe_2)_2$ (A) and the observed ^{13}C NMR spectrum (at 14.05 MHz) of $(PhPSiMe_2)_3$ containing some $(PhPSiMe_2)_2$ as an impurity (B). A computer simulation of the ^{13}C NMR spectrum of $(PhPSiMe_2)_3$ (with ^2J(PC) 12.33 Hz, ^4J(PC) 1.46 Hz, and J(PP') 20 Hz) is shown in (C) using the NMR simulation program NUMARIT provided by Dr. J.S. Martin of the University of Alberta.

The variation in ^2J(PC) is less uniform. The decrease in its value along the series $PhP(SiMe_2)_{4,5,6}$ can be attributed to an expected decrease in the P—Si—C angle in the larger rings [25], but the near equivalence of ^2J(PC) for $(PhPSiMe_2)_n$ (n = 2, 3) and the low value of ^2J(PC) in $[PhP(SiMe_2)_2]_2$ are less easily explained. The deviations from regularity probably arise from the fact that the value of ^2J(PC) depends on the hybridization at phosphorus as well as the P—Si—C angle. Since the Si—P—Si and P—Si—C angles will vary in opposite senses with change in ring size, the net effect is not likely to produce a simple dependence of ^2J(PC) on the number of atoms in the ring.

The ^1H and ^{13}C chemical shifts of the methyl groups in $(PhP)_m(SiMe_2)_n$ are consistent with the trends expected by the replacement of one or more silicon atoms of a cyclic polysilane by phosphorus. For the series $PhP(SiMe_2)_n$ (n = 4, 5, 6) the β- and γ-methyl groups exhibit chemical shifts similar to those found in the parent polysilanes $(Me_2Si)_{n+1}$ (Table 2), while the resonances of

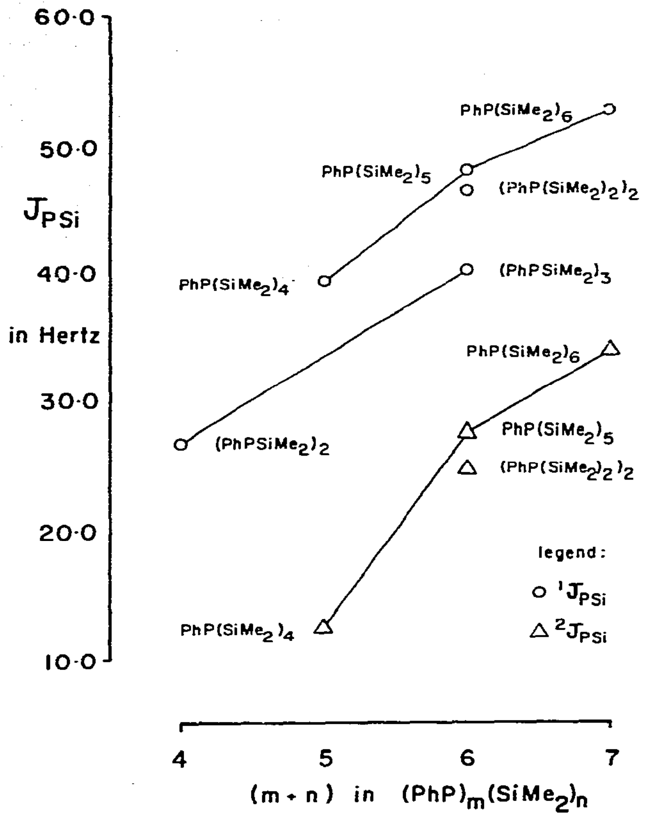


Fig. 4. $^1J(PSi)$ and $^2J(PSi)$ coupling constants of $(PhP)_m(SiMe_2)_n$ as a function of ring size $(m + n)$.

the α-methyl groups are moved downfield from these values, as expected from their proximity to the more electronegative phosphorus atom. When more than one phosphorus atom is present, the methyl groups in $(PhPSiMe_2)_{2,3}$ and $[PhP(SiMe_2)_2]_2$ are even more deshielded. This deshielding effect appears to be general for all the compounds studied, with variations in ring size having little effect on the chemical shift of any particular type of methyl group. Although this deshielding could arise from an enhanced σ-inductive effect, this is not the normal explanation for β-effects in ^{13}C NMR. An alternative explanation is a loss in the shielding effect attributed to γ-interactions which results from the replacement of $SiMe_2$ groups by PPh groups.

TABLE 2

^1H, ^{13}C AND ^{29}Si NMR CHEMICAL SHIFTS [a] OF THE CYCLIC PERMETHYLPOLYSILANES $(SiMe_2)_n$

	5	6	7
δ(H)	0.21	0.20	0.21
δ(C)	−6.28	−5.97	−5.20
δ(Si)	−42.13	−41.87	−41.68

[a] δ (in ppm), in C_6D_6 solution, reference internal TMS.

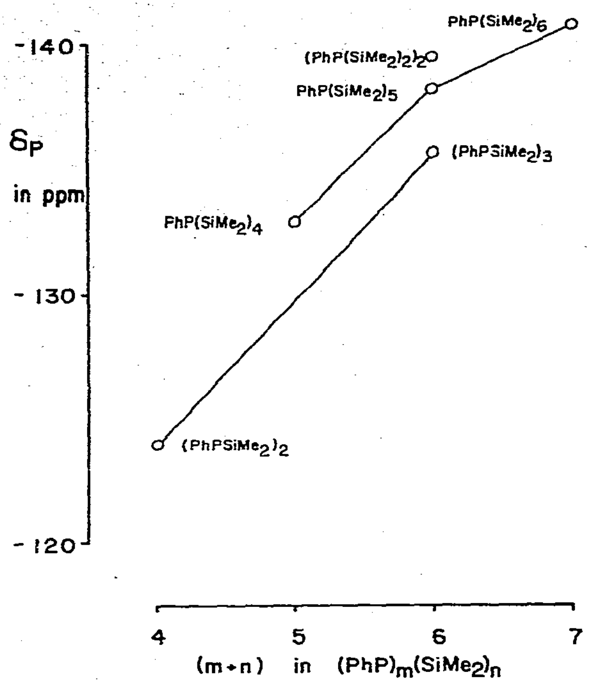
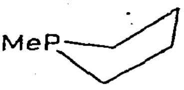


Fig. 5. ^{31}P chemical shifts of $(PhP)_m(SiMe_2)_n$ as a function of ring size $(m + n)$.

The trends in the ^{29}Si chemical shifts can be interpreted similarly, the resonance of the β- and γ-silicon atoms being only slightly different from the values found in the homonuclear polysilanes, while the α-silicon atoms show an increased deshielding which is approximately proportional to the number of adjacent phosphorus atoms. For the series $PhP(SiMe_2)_n$ ($n = 4, 5, 6$) the effect of ring size is more noticeable, but it is difficult to establish at this point whether the variation in $\delta(Si_\alpha)$ along the series $n = 4, 5, 6$ is due to angular effects or to more effective $p\pi \rightarrow d\pi$ donation from phosphorus to silicon in the larger rings, or both.

The ^{31}P chemical shifts of the P_mSi_n rings are shown in Fig. 5, plotted as a function of $(m + n)$. Viewing the results in a qualitative fashion, the small increases in shielding along the series $PhP(SiMe_2)_n$ ($n = 4, 5, 6$) and between $(PhPSiMe_2)_n$ for $n = 2$ and 3 parallels the larger difference observed between the phosphorinane V ($\delta(P)$ —53.7 ppm) [18] and the phospholane VI ($\delta(P)$ —32 ppm) [26]. For the latter two compounds, the unusually large shielding



(VI)

in the 6-membered ring V has been attributed to the steric influence of the γ-carbon atom [29]. In the present series, a similar γ-effect may account for the greater shielding found in $PhP(SiMe_2)_{5-6}$, but other factors must also be considered. The low shielding in $PhP(SiMe_2SiMe_3)_2$ (δ(P) −124.7 ppm) as compared to $PhP(SiMe_3)_2$ (δ(P) −137.4 ppm [30]) can be attributed to the presence of the β-silicon atoms in the former, an analogous effect being observed when β-carbon atoms are present in alkylphosphines [29]. Cyclization of $PhP(SiMe_2SiMe_3)_2$ to $PhP(SiMe_2)_4$ results in an upfield shift in δ(P), which we interpret as the result of a more constricted angle at phosphorus in the cyclic molecule [31]. In the absence of other factors a gradual decrease in shielding would then be expected along the series $PhP(SiMe_2)_{4,5,6}$, the angle at phosphorus being wider in the larger rings. The observed trend in chemical shifts is therefore the net result of the opposing effects of angular variations and γ-steric interactions, the latter apparently being the more important *.

Infrared spectra

Because of the large number of methyl and phenyl substituents in these molecules, their infrared spectra are difficult to interpret in detail. The most informative region lies between 300—600 cm^{-1}, and contains only the skeletal vibrations of the P—Si and Si—Si bonds. The presence of one or more phosphorus atoms in these compounds lowers the high symmetry of the parent polysilanes, and the single ν(Si—Si) band found in these compounds ($n = 5$, 400 cm^{-1}; $n = 6$, 383 cm^{-1}; $n = 7$, 362 cm^{-1}) [32] is split into a number of bands in the phosphasilanes, the strongest occurring between 486 and 460 cm^{-1}. This vibration probably corresponds to ν_{asym}(P—Si), the equivalent vibration in $(Me_3Si)_3P$ being found at 461 cm^{-1} [33].

The molybdenum tricarbonyl complex of $(PhPSiMe_2)_3$ gives rise to two ν(CO) bands (A + E) at 1925 and 1830 cm^{-1} (in THF solution). These frequencies are similar to those found in $(PhPSiPh_2)_3Mo(CO)_3$ (1931, 1838 cm^{-1}) [5], but lower than in *fac*-alkyl- and -aryl-phosphinemolybdenum tricarbonyl complexes [34—36]. As expected from the low electronegativity of silicon, the Si_3P_3 ligand is a poor π-acceptor of electron density from molybdenum.

Experimental

The linear α,ω-dichloropermethylpolysilanes $Cl(SiMe_2)_nCl$ ($n = 2$—4, 6) were prepared by the chlorination of dodecamethylcyclohexasilane $(SiMe_2)_6$ with chlorine [2,3]. The 1,5-dichloropentasilane $Cl(SiMe_2)_5Cl$ was prepared similarly starting from decamethylcyclopentasilane $(SiMe_2)_5$ [3]. The dichlorosilanes so formed were separated by fractional distillation in vacuo or by preparative VPC (for $n = 5$) using a 3/8″ × 6′ QF-1 column (20% on Chromosorb W, 60—80 mesh). The monochlorodisilane $Me_3SiSiMe_2Cl$ was prepared by the chlorodemethylation of hexamethyldisilane [12]. Dodecamethylcyclohexasilane $(SiMe_2)_6$ was prepared by the condensation of dichlorodimethylsilane with sodium/potassium alloy [10], and decamethylcyclopentasilane $(SiMe_2)_5$ prepared from it by photolysis at 2537 Å for 24 h (approximate conversion = 30%) [37]. Phenylphosphine was prepared by the reduction of dichlorophenylphosphine with

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* In the phosphadicarbadisilane IV, the absence of β-silicon atoms and the expectedly small angle at phosphorus combine to produce a large shielding effect, and δ(P) (−170.5 ppm) [8] is to high field of all the compounds reported here.

lithium aluminum hydride [38] and cycloheptatrienylmolybdenum tricarbonyl by the reaction of molybdenum hexacarbonyl with cycloheptatriene [39].

Dichlorophenylphosphine, dichlorodimethylsilane, molybdenum hexacarbonyl and cycloheptatriene were all commercial products. All were used without further purification except dichlorodimethylsilane, which was redistilled prior to use. 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 titration with hydrochloric acid. Tetrahydrofuran was dried by distillation from potassium, and benzene by distillation from lithium aluminum hydride.

Unless otherwise stated, ^{1}H NMR spectra were recorded on a JEOL MH-100 NMR spectrometer, and ^{13}C, ^{29}Si and ^{31}P NMR spectra were obtained using a Varian XL-100 NMR spectrometer operating in the FT mode. Infrared spectra were recorded from samples in Nujol mulls using a Perkin—Elmer 457 grating spectrophotometer. Mass spectra were recorded on an AEI type MS 902 mass spectrometer, samples being admitted through conventional inlet systems *. Elemental analyses were performed by M.H.W. Laboratories, Garden City, Michigan.

It should be noted that the phosphorus—silicon heterocycles reported here are extremely sensitive to oxygen and moisture, rapidly evolving the odor of phenylphosphine upon exposure to air. The compound $(PhSiMe_2)_{2,3}$ will inflame in air if spread thinly on a piece of tissue paper.

Preparation of dilithium phenylphosphide

Dilithium phenylphosphide was prepared in situ by the slow addition (via syringe and septum) of two equivalents of n-butyllithium in hexane to a solution of phenylphosphine in tetrahydrofuran. The canary yellow slurry of dilithium phenylphosphide thus formed was stirred under an atmosphere of nitrogen for one hour before use.

Preparation of $PhP(SiMe_2)_n$ (n = 4, 5, 6)

A solution of the dichloropermethylpolysilane $Cl(SiMe_2)_nCl$ (n = 4, 5, 6) in approximately 20 ml of tetrahydrofuran was added dropwise under an atmosphere of nitrogen to a slurry of freshly prepared dilithium phenylphosphide in 100 ml of tetrahydrofuran at room temperature. Upon completion of the addition, the colorless solution so formed was left to stir overnight to ensure the completion of the reaction. The mixture was then heated under reflux for one hour, effecting the precipitation of lithium chloride. The mixture was cooled and filtered, and the solvent distilled off from the filtrate to leave a pale yellow oil which was distilled in vacuo through a 6″ Vigreux column packed with glass helices. The crude product so obtained was further purified for analytical purposes by a second distillation in vacuo.

$PhP(SiMe_2)_6$. Using the above procedure, the reaction of $Cl(SiMe_2)_6Cl$ (1.73 g, 4.14 mmol) with Li_2PPh (from 0.455 g, 4.14 mmol phenylphosphine) yielded $PhP(SiMe_2)_6$ (1.41 g, 3.08 mmol, yield 76%) as a colorless liquid, b.p. 165—168°C/

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* We are grateful to Professor N.L. Paddock and Dr. G. Eigendorf of the University of British Columbia for running the mass spectra of $PhP(SiMe_2)_n$ (n = 4, 5, 6).

0.04 Torr. Anal. Found: C, 47.06; H, 8.84; P, 6.55. $C_{18}H_{41}PSi_6$ calcd.: C, 47.31; H, 9.04; P, 6.78%. High resolution mass number Found: 456.1546, calcd. for $C_{18}H_{41}PSi_6$: 456.1552. IR spectrum (300—600 cm^{-1} region): 500w, 486m, 452m, 414vw, 335w, 340vw.

$PhP(SiMe_2)_5$. Using the same procedure, the reaction of $Cl(SiMe_2)_5Cl$ (2.11 g, 5.93 mmol) with Li_2PPh (from 0.651 g, 5.93 mmol phenylphosphine) yielded $PhP(SiMe_2)_5$ (1.95 g, 4.87 mmol, yield 80%) as a colorless crystalline solid, b.p. 146°C/0.03 Torr, m.p. 64—68°C. Anal. Found: C, 48.04; H, 8.83; P, 7.55. $C_{16}H_{35}PSi_5$ calcd.: C, 48.18; H, 8.84; P, 7.77%. High resolution mass number Found: 398.1331, calcd. for $C_{16}H_{35}PSi_5$: 398.1328. IR spectrum (300—600 cm^{-1} region): 486w, 460m, 430w, 382w, 365w.

$PhP(SiMe_2)_4$. Using the same procedure, the reaction of $Cl(SiMe_2)_4Cl$ (2.57 g, 8.48 mmol) with Li_2PPh (from 0.933 g, 4.48 mmol phenylphosphine) yielded $PhP(SiMe_2)_4$ (1.90 g, 5.57 mmol, yield 66%) as a colorless liquid, b.p. 105—107°C/ 0.03 Torr, m.p. 6—10°C. Anal. Found: C, 49.12; H, 8.79; P, 9.12. $C_{14}H_{29}PSi_4$ calcd.: C, 49.35; H, 8.58; P, 9.09%. High resolution mass number Found: 340.1061 calcd. for $C_{14}H_{29}PSi_4$: 340.1069. IR spectrum 300—600 cm^{-1} region): 480w, 460m, 440w, 399w, 385w.

Attempted preparation of $PhP(SiMe_2)_3$

A solution of $Cl(SiMe_2)_3Cl$ (3.56 g, 14.5 mmol) in 20 ml of tetrahydrofuran was added dropwise under an atmosphere of nitrogen to a slurry of dilithium phenylphosphide (from 1.59 g, 14.5 mmol phenylphosphine) in 150 ml of tetrahydrofuran. The yellow precipitate disappeared to leave a colorless solution. After about 15 min a creamy white precipitate began to form and after 24 h, the mixture had the consistency of a paste. Filtration of the mixture proved extremely difficult, and only about 3/4 of the filtrate was effectively recovered. Removal of the solvent from this solution yielded a small (~0.5 ml) amount of a yellow oil, which was not further characterized. The insoluble material (probably polymeric), therefore comprised the major part of the product.

Preparation of $[PhP(SiMe_2)_2]_2$

A solution of $Cl(SiMe_2)_2Cl$ (4.85 g, 25.9 mmol) in 50 ml of tetrahydrofuran was added dropwise under an atmosphere of nitrogen to a slurry of freshly prepared dilithium phenylphosphide (from 2.85 g, 25.9 mmol phenylphosphine) in 200 ml of tetrahydrofuran at —23°C (CCl_4/dry ice slush bath). When the addition was complete the mixture was allowed to warm to room temperature and then left to stir under nitrogen overnight. The following day the solution was heated under reflux for 1 h to induce precipitation of lithium chloride. The mixture was then cooled and filtered, and the solvent removed by distillation to leave a white solid, which was distilled in vacuo using an air-cooled condenser to give a white crystalline solid $[PhP(SiMe_2)_2]_2$ (4.06 g, 9.10 mmol, yield 70%), b.p. 185—190°C/0.03 Torr, m.p. 148—151°C (recrystallized as microcrystalline feathers from hot hexane). Anal. Found: C, 53.37; H, 7.58; P, 13.75. $C_{20}H_{34}P_2Si_4$ calcd.: C, 53.53; H, 7.64; P, 13.80%. High resolution mass number Found: 448.1187, calcd. for $C_{20}H_{34}P_2Si_4$: 448.1203. IR spectrum (300—600 cm^{-1} region): 480ms, 455w, 392w, 305w.

Preparation of *$(PhPSiMe_2)_2$*

A solution of Me_2SiCl_2 (5.00 g, 38.8 mmol) in 50 ml of tetrahydrofuran was added dropwise under nitrogen to a slurry of dilithium phenylphosphide (from 4.23 g, 38.8 mmol phenylphosphine) in 250 ml of tetrahydrofuran at —40°C (CH_3CN/dry ice slush bath) and the mixture stirred for 1 h at this temperature, and then left to stir overnight at room temperature. The following day, the mixture was heated under reflux for 1 h, then cooled and filtered, and the solvent distilled in vacuo to yield $(PhPSiMe_2)_2$ (3.88 g, 11.6 mmol, yield 62%), a colorless crystalline solid, b.p. 175—190°C/0.03 Torr, m.p. 90—93°C (recrystallized as square plates from benzene/hexane (50/50)). Anal. Found: C, 57.52; H, 6.80; P, 18.87. $C_{16}H_{22}P_2Si_2$ calcd.: C, 57.80; H, 6.67; P, 18.63%. High resolution mass number Found: 332.0736, calcd. for $C_{16}H_{22}P_2Si_2$: 332.0755. IR spectrum (300—600 cm^{-1} region): 492(sh), 485ms, 478(sh), 452vw, 400ms, 360ms.

Preparation of *$(PhPSiMe_2)_3$*

A solution of Me_2SiCl_2 (5.13 g, 39.8 mmol) in 50 ml of tetrahydrofuran was added dropwise under nitrogen to a slurry of dilithium phenylphosphide (from 4.37 g, 39.8 mmol phenylphosphine) at room temperature. The ensuing reaction was sufficiently exothermic to raise the temperature of the mixture to about 40°C. After the addition was complete, the mixture was left to stir overnight at room temperature. The solution was heated under reflux for 1 h, then cooled and filtered, and the solvent distilled from the filtrate to leave a yellow oil which was fractionally distilled in vacuo through a 6" Vigreux column packed with glass helices. The first fraction was an off-white semisolid (~0.35 ml, b.p. 90—183°C/0.01 Torr). The second fraction distilled off at 230—233°C/0.01 Torr to give $(PhPSiMe_2)_3$ (4.5 g, 9.0 mmol, yield 70%), a pale yellow viscous gum which softened to a mobile liquid at temperatures above 80°C. Anal. Found: P, 18.20 *. $C_{24}H_{33}P_3Si_3$ calcd.: P, 18.63%. High resolution mass number Found: 498.1081, calcd. for $C_{24}H_{33}P_3Si_3$: 498.1103. IR spectrum (300—600 cm^{-1} region): 478ms, 440vw, 405w, 380vw.

Preparation of *$(PhPSiMe_2)_3Mo(CO)_3$*

A slight molar excess of $(PhPSiMe_2)_3$ (0.73 g, 1.48 mmol) in 10 ml of benzene was added under an atmosphere of argon to a stirred solution of cycloheptatrienylmolybdenum tricarbonyl (0.359 g, 1.32 mmol), in 125 ml of benzene. The cherry red solution was warmed to 60°C, whereupon a canary yellow precipitate began to form in the mixture. Heating was then halted, and the mixture left to stir at room temperature for 4 h. The yellow air-sensitive solid $(PhPSiMe_2)_3Mo(CO)_3$ (0.472 g, 0.62 mmol, yield 47% based on molybdenum) was filtered from the solution and recrystallized from a hot tetrahydrofuran/benzene mixture (50/50) as small yellow needles, dec. > 1 90°C. Anal. Found: C, 47.58; H, 4.76; P, 13.77. $C_{27}H_{33}P_3Si_3O_3Mo$ calcd.: C, 47.77; H, 4.90; P, 13.69%. High resolution mass number Found: 679.9959, $C_{27}H_3P_3Si_3O_3Mo$ calcd.: 680.0009. IR spectrum

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* Difficulties with sample handling prevented a satisfactory analysis for carbon and hydrogen. The compound was further characterized as its molybdenum tricarbonyl complex.

(300—600 cm^{-1} region): 598ms, 553m, 507vw, 479w, 460m, 450m, 386m. Carbonyl region 1910, 1810 (nujol mull); 1925, 1830 cm^{-1} (THF solution).

Preparation of $PhP(SiMe_2SiMe_3)_2$

A solution of $Me_3SiSiMe_2Cl$ (6.72 g, 4.66 mmol) in 20 ml of tetrahydrofuran was added dropwise under an atmosphere of nitrogen to a slurry of dilithium phenylphosphide (from 2.59 g, 2.33 mmol of phenylphosphine) in 200 ml of tetrahydrofuran, and the resulting colorless solution allowed to stir overnight at room temperature. The following day the mixture was refluxed for 1 h, then filtered, and the solvent distilled off from the filtrate to leave an oil which was distilled in vacuo through a 6″ Vigreux column to give $PhP(SiMe_2SiMe_3)_2$, a colorless liquid, b.p. 115—117°C/0.1 Torr. Anal. Found: C, 51.60; H, 9.76; P, 8.57. $C_{16}H_{35}Si_4P$ calcd.: C, 51.83; H, 9.52; P, 8.35%. High resolution mass number Found: 370.15491, calcd. for $C_{16}H_{35}PSi_4$: 370.15535. IR spectrum (300—600 cm^{-1} region): 465m, 392vw.

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References

1 T.F. Block, M. Biernbaum and R. West, J. Organometal. Chem., 131 (1977) 199.
2 W. Wojnowski, C.J. Hurt and R. West, J. Organometal. Chem., 124 (1977) 271.
3 H. Gilman and S. Inoue, J. Organometal. Chem., 15 (1968) 237.
4 G.W. Parshall and R.V. Lindsey, J. Amer. Chem. Soc., 81 (1959) 6273.
5 H. Schumann and H. Benda, Angew. Chem. Int. Ed., 9 (1970) 76; Chem. Ber., 104 (1971) 333.
6 G. Fritz and W. Hölderich, Z. Anorg. Allg. Chem., 431 (1977) 76.
6(a) Unpublished work by F. Höfler and P. Wolfer, reported in E. Hengge, Topics in Current Chemistry, 51, Springer-Verlag, New York, 1974, p. 87.
7 E. Hengge and U. Brychcy, Monatsh. Chem., 97 (1966) 1309.
8 C. Couret, J. Satgé, J. Escudié and J.D. Andriamizaka, J. Organometal. Chem., 132 (1977) C5.
9 A.W. Cordes, R. Oakley and P.F. Schubert, to be published.
10 E. Carberry and R. West, J. Organometal. Chem., 6 (1966) 582; J. Amer. Chem. Soc., 91 (1969) 5440.
11 T. Newman, R.T. Oakley and R. West, unpublished results.
12 M. Kumada, M. Yamaguchi, Y. Yamamoto, J. Nakajima and K. Shiina, J. Org. Chem., 21 (1956) 1264.
13 U. Wannagat, H. Autzen and M. Schlingmann, Z. Anorg. Allg. Chem., 419 (1976) 41.
14 U. Wannagat and O. Brandstätter, Monatsh. Chem., 94 (1963) 1090.
15 E. Wiberg and D. Dathe, Diplomarbeit Thesis, München 1955; quoted in Gmelins Handbuch der Anorganischen Chemie, Verlag Chemie GmbH, Weinheim, 1958, Silicon, Part C, p. 306.
16 K. Moedritzer, J.R. van Wazer and C.H. Dungan, J. Chem. Phys., 42 (1965) 2478.
17 K. Moedritzer, J. Organometal. Chem., 21 (1970) 315.
18 S.I. Featherman and L.D. Quin, J. Amer. Chem. Soc., 95 (1973) 1699.
19 A.J. Carty and R.K. Harris, Chem. Commun., 234 (1967).
20 R.K. Harris, Can. J. Chem., 42 (1964) 2275.
21 J.W. Emsley, J. Feeney and L.H. Sutcliffe, High Resolution NMR Spectra, Pergamon Press, Oxford, 1966, p. 1061—1068.
22 R.J. Abraham, E.O. Bishop and R.E. Richards, Mol. Phys., 3 (1960) 485.
23 P. Diehl and J.A. Pople, Mol. Phys., 3 (1961) 557.
24 H.M. McConnell, J. Chem. Phys., 24 (1956) 460.
25 G.S. Gutowsky, M. Karplus and D.M. Grant, J. Chem. Phys., 31 (1959) 1278.

26 K.D. Summerhays and D.A. Deprez, J. Organometal. Chem., 118 (1976) 19.
27 R.N. Knibbs, D.A. Stanislawski and R. West, unpublished results.
28 J.J. Breen, J.F. Engel, D.K. Myers and L.D. Quin, Phosphorus, 2 (1972) 55.
29 L.D. Quin and J.J. Breen, Org. Magn. Res., 5 (1973) 17.
30 H. Schumann and H.-J. Kroth, Z. Naturforsch. B, 32 (1977) 513.
31 J.H. Letcher and J.R. Van Wazer, in M. Grayson and E.J. Griffith (Eds.), Topics in Phosphorus Chemistry, John Wiley and Sons, New York, 1967, Vol. 5, Chap. 2.
32 E. Carberry, R. West and G.E. Glass, J. Amer. Chem. Soc., 91 (1969) 5446.
33 H. Bürger and U. Goetze, J. Organometal. Chem., 12 (1968) 451; Spectrochim. Acta, 26A (1970) 671.
34 F.A. Cotton, Inorg. Chem., 3 (1964) 702.
35 R.B. King, R.N. Kapoor, M.S. Saran and P.N. Kapoor, Inorg. Chem., 10 (1971) 1851.
36 E.P. Kyba, C.W. Hudson, M.J. McPhaul and A.M. John, J. Amer. Chem. Soc., 99 (1977) 8053.
37 M. Ishikawa and M. Kumada, Chem. Commun., (1970) 612.
38 F. Fass and H. Schindlbauer, Monatsh. Chem., 90 (1959) 148.
39 R.B. King, in J.J. Eisch and R.B. King (Eds.), Organometallic Synthesis, Academic Press, New York, 1965, Vol. 1, p. 125.